INFLUENCE OF CARBON NANOTUBES (CNT) ON THE MECHANICAL PROPERTIES OF THE POLYETHYLENE THERAPHTHALATE (PET)/CNT NANOCOMPOSITE FIBERS

BY

MOHAMMED RIYAZUDDIN FAROOQUI

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This thesis, written by Mohammed Riyazuddin Farooqui under the direction of his thesis advisor and approved by his thesis committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE in MECHANICAL ENGINEERING.**

Thesis Committee

Dr. Khaled Mezghani (Advisor)

Dr. Saheb Nouari (Member)

Dr. Tahar Laoui (Member)

Dr. Amro M. Al- Qutub
Department Chairman

Dr. Salam A. Zummo
Dean of Graduate Studies

8/5/12

Date

Dedicated to

My beloved parents, brothers and sisters for their duas and constant support and encouragement throughout my life

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THESIS ABSTRACT (ENGLISH)

NAME: MOHAMMED RIYAZUDDIN FAROOQUI

TITLE: INFLUENCE OF CARBON NANOTUBE (CNT) ON THE MECHANICAL PROPERTIES AND PROCESSIBLITY OF POLYETHYLENE TERAPHTHALATE (PET)/CNT NANOCOMPOSITE FIBERS

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Polyethylene teraphthalate (PET) is one of the mostly used polyester for fiber production. It is spun into filament, string or rope and used as a component of composite materials. In order to enhance their strength and broaden their application, PET fibers are blended with carbon nanotubes (CNT) which are known for high strength and stiffness. However, to produce good quality of PET/CNT nanocomposite fibers two major challenges were faced, one to obtain good distribution of CNT and the other to achieve good alignment of CNT along the fiber direction. In the present work, good distribution of CNT in PET matrix was achieved using twin screw melt extrusion process and the CNT alignment was obtained using melt spinning technique. The present study investigated the effect of process parameters on the mechanical properties of two sets of fibers. The first set of fibers is extruded in the form of large diameter fibers in the range of 220 to 700µm. The second set of fibers was melt spun into fine fibers of diameter in the range of 20 to 50 µm.

The extruded fibers showed good improvement in their mechanical properties with respect to CNT content in the range of 0.1 to 7.5wt%. The highest improvement of

mechanical properties was achieved with 0.1 wt% CNT content. Using this concentration in the nanocomposite fibers, the tensile strength was enhanced by about 90%, compared to pure PET fibers (51MPa). In addition, this composition significantly enhanced the strain at break by about 173 % and toughness by about 285 %. Other CNT concentration showed moderate improvements.

The second set of fibers which were melt spun fibers also showed good enhancement in the strength, stiffness and toughness with respect to CNT content in the range of 0.1 to 2.7wt%. The best improvement in the mechanical properties was observed with 0.1 and 0.5wt% CNT. Incorporating 0.1 and 0.5 wt% CNT in spun PET/CNT nanocomposite fibers of 20 µm diameters showed remarkable increment in the modulus by about 16% and 56%, respectively, compared to pure PET fibers with a modulus of 8.6 GPa. The tensile strength of PET/CNT nanocomposite fibers improved by about 40% (532MPa) due to the addition of 0.1wt% CNT in PET/CNT nanocomposite, compared to pure PET fibers of 380MPa. In addition, incorporating 0.1wt% CNT content in PET/CNT nanocomposite fibers of 50 µm diameter resulted in good improvement in toughness i.e. about 26% (689MPa). The improvements in the mechanical properties were based on the good mixing, distribution and alignment of CNT in PET/CNT nanocomposite fibers, as observed with scanning electron microscope

MASTER OF SCIENCE DEGREE
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
Dhahran, Saudi Arabia

THESIS ABSTRACT (ARABIC)

الاسم:.. *محمد رياض الدين فاروقي*

العنوان: *تأثير أنابيب النانو الكربونية (سي إن تي) على الخواصّ الميكانيكيّة و القدرة العملية للبولي اثيلين تيرافثالات (بي إي تي) ذات الألياف (سي إن تي) نانوية التركيب.*

التخصص: *الهندسة الميكانيكية .*

التاريخ: مارس 2012

البولي ايثيلين تيرافثالات (بي إي تي) هو من اهم المركبات البولي استيرية لصناعة الألياف. حيث تنسج الى خيوط أو حبال لتستخدم بعد ذلك كعنصر للمواد المركبة. و من أجل تعزيز قوتها و توسيع مجالات الاستعمال بها يمزج ال(بي إي تي) مع أنابيب النانو الكربونية (سي إن تي) حيث تعرف هذه الأنابيب بقوتها و قدرتها على التحمل العاليتين. ولكن حتى ننتج جودة عالية من هذه الألياف نانوية التركيب واجهنا اثنين من المصاعب الرئيسية. الأول هو الحصول على التوزيع الجيد لل(سي إن تي) و الثاني هو السعي وراء تحقيق المواءمة الجيدة لل (سي إن تي) على نفس اجاه الألياف. في الوقت الحالي تم تحقيق التوزيع الجيد لل(سي إن تي) في ال(بي إي تي) من خلال اجراء عملية twin screw melt extrusion process و تم تحقيق مواءمة ال (سي إن تي) من خلال اجراء تقنية غزل المذاب. الدراسة الحالية ناقشت تأثير عملية المعالم على الخصائص الميكانيكية من مجموعتين من الألياف. المجموعة الاولى تقذف على شكل ألياف كبيرة القطر في مدى 220 الى 700 µm. المجموعة الثانية غزل مصهورها الى ألياف دقيقة بأقطار في مدى 20 إلى 50 µm.

الألياف المقذوفة اظهرت تحسن ملحوظ في خواصها الميكانيكية بالنسبة الى نسبة ال(سي إن تي) في المركب من 0.1 الى 7.5 وزن%. أعلى معدل تحسن في الخواص الميكانيكية تم الحصول عليها في مركب 0.1 وزن % من ال (سي إن تي) . بإستخدام هذه النسبة من التركيز في الألياف نانوية التركيب، قوة الشد تحسنت بمقدار % 90، مقارنة مع ال(بي إي تي) النقي (51 MPa). أيضا هذا التركيز حّسن بشكل كبير كلٌ من التوتر عند الكسر بنسبة % 173 و الصلابة بنسبة % 285. نسب التركيز الأخرى لل(سي إن تي) أظهرت معدلات تحسن معتدلة.

المجموعة الثانية من الألياف التي غزل مصهورها هي الأخرى أظهرت تحسن جيد في القوة, القساوة و الصلابة بالنسبة لتركيز ال(سي إن تي) في المدى 0.1 الى 2.7 وزن %. أفضل التحسنات في الخواص الميكانيكية لوحظت في 0.1 و0.5 وزن % من (سي إن تي) . مزج 0.1 و 0.5 وزن% من ال(سي إن تي) في (بي إي تي)\(سي إن تي) ألياف نانوية التركيب ذات قطر 20 µm أظهرت زيادة ممتازة في معامل. بنسبة% 16 و % 25 على الترتيب. مقارنة مع ألياف(بي إي تي) النقية ذات معامل يونج بمقدار 8.6 GPa. قوة الشد لألياف(بي إي تي)\(سي إن تي) نانوية التركيب تحسنت بمقدار % 40 (532 MPa) نظرًا لزيادة 0.1 وزن % من (سي إن تي) في (بي إي تي)\(سي إن تي) نانوية التركيب، مقارنة بألياف (بي إي تي) النقية بمقدار 380 MPa . أيضًا ، مزج 0.1 وزن% من (سي إن تي) الى ألياف(بي إي تي)\(سي إن تي) نانوية التركيب ذات قطر 50 µm نتج عن ذلك تحسن جيد في الصلابة % 26 (689 MPa). التحسنات في الخواص الميكانيكية بنيت على اساس المزج الجيد، التوزيع و المواءمة لل(سي إن تي) في ألياف (بي إي تي)\(سي إن تي) نانوية التركيب، كما لوحظ بإستخدام المجهر الألكتروني.

درجة الماجستير في العلوم

جامعة الملك فهد للبترول و المعادن

الظهران المملكة العربية السعودية

CHAPTER 1

INTRODUCTION

1.1 Research Background

1.2 PET

At the end of nineteenth century, only natural fibers such as cotton, wool, and silk were available[1]. Later new classes of fibers made from polymer and ceramics were developed. In the class of polymeric fibers, these include polyester, nylon, polyethylene, polypropylene, acrylic, spandex, Nomex®, Kevlar®, and Zylon®. The class of other fibers includes carbon fibers, silicon carbide, alumina, glass, alumina-borosilicate, and boron. The first man-made fiber was Nylon which replaced the silk in parachutes and military uses.

Today, the polyester industry makes up about 18% of world polymer production and is third after polyethylene (PE) and polypropylene (PP). Of all the other type of polyester the most significant in fibers production is Polyethylene teraphthalate (PET), its repeating unit is shown in Figure 1.1. PET was first developed by Whinfield and Dickson in 1939[2] by chemical reaction between teraphthalic acid (TPA) and ethyl glycol (EG)

shown in Figure 1.2 (known as poly condensation process). PET is a stiff, hard, strong, has good gas barrier properties and good chemical resistance except to alkalis. Its crystallinity varies from amorphous to fairly high crystalline. It can be vastly transparent and colorless [3].

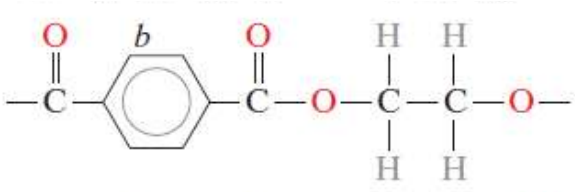

Figure 1.1 Repeating unit of PET

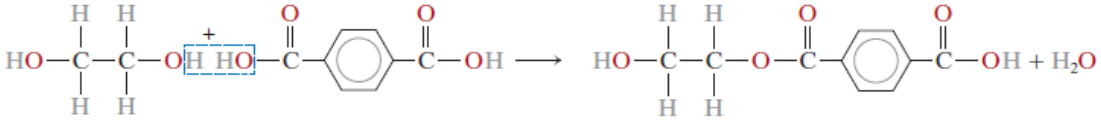

Figure 1.2 Polymer condensation

Thermal and mechanical properties of the PET are shown in Table 1.1. Molecular weight of repeat unit is 192.2 g/mol. [3]. Pattabiraman et.al [4] has shown that mechanical properties of virgin PET had the strength of 57MPa and modulus of elasticity of 2.3GPa. Another research group[5] has spun the PET Fibers, of size 21µm to 27 µm, through twin Screw extruder and they reported the tensile strength of 350MPa to 510 MPa and the young modulus was in the range of 7 GPa to 13 GPa. Hence, Owing to its versatile properties, it has found applications in textile, automobile and in shipping industry.

Globally the production of PET synthetic fibers is 60 % of the world's PET production. It has been seen that several fine synthetic PET fibers are used for manufacturing mooring ropes which are used in ships [6-7]. PET also found significant used in construction industry as concrete-reinforcing fiber [8]. Moreover, PET is produced locally in Saudi Arabia in large quantity. Hence, enhancing the mechanical strength of PET can also improve the economy of the local market of the Saudi Arabia. In addition, PET with improved properties can be used in variety of industrial and household applications. They can be spun into filaments, string or rope, used as a component of composite materials. Efforts are being made to increase the range of applications of PET nanocomposites fibers, such as in medicine, electronics, biomaterials and energy production. The enhancement in the properties of PET composite fibers is achieved by modifying with organic and inorganic nanomaterials (1nm to 100nm) [19-36]. Nanomaterials include carbon nanotubes (CNT), carbon nanofiber, nanoclay, nanosilica and others.

1.3 CNT

CNT were first reported by Iijima in the year 1991[9]. After that, many investigations and developments are taking place to understand the full ability of CNT. In addition, it has been observed that CNT are ideal material for PET fiber reinforcement[10]. They are hexagonal network of carbon graphene sheets rolled into seamless cylinder with caps at the ends which are composed of half of the fullerene molecule. CNT are produced as single wall-CNT(SWCNT) Figure 1.3 or Multi wall-CNT shown in Figure 1.4. They are highly isotropic[11]. It was predicted that even the weak carbon nano tubes have the

strength in the order of several giga Pascals and young's modulus in the tera Pascal's [12] with low weight. In addition, CNTs have unique electrical properties and are good conductors of heat which make them novel material in various fields such as electrical field, nanotechnology, aerospace & material science [11].

Table 1.1 Characteristics of PET [4]

Melting temperature	250˚C
Glass transition temperature	76˚C
Crystallinity	33%
Tensile strength	Bulk 57 MPa
young modulus	2321.59MPa
Molecular weight of repeat unit	192.2 g/mol
PET Fibers [5]	
Fiber diameter	21 µm to 27 µm
Young's modulus	7GPa to 13GPa
Tensile strength	350MPa to 510MPa

The diameter of the nanotubes ranges from 1nm-100nm and length in millimeters and their density 1.3 gm/cm3 [13-14]. Young modulus measured to be 1.25TPa [12, 14] i.e. five times stiffer than that of the steel (210 GPa) and among all the properties of CNTs, the tensile strength that make them apart from other material were observed to be 63GPa i.e. fifty times stronger than the steels. Table 1.2 summarizes the CNTs' characteristics.

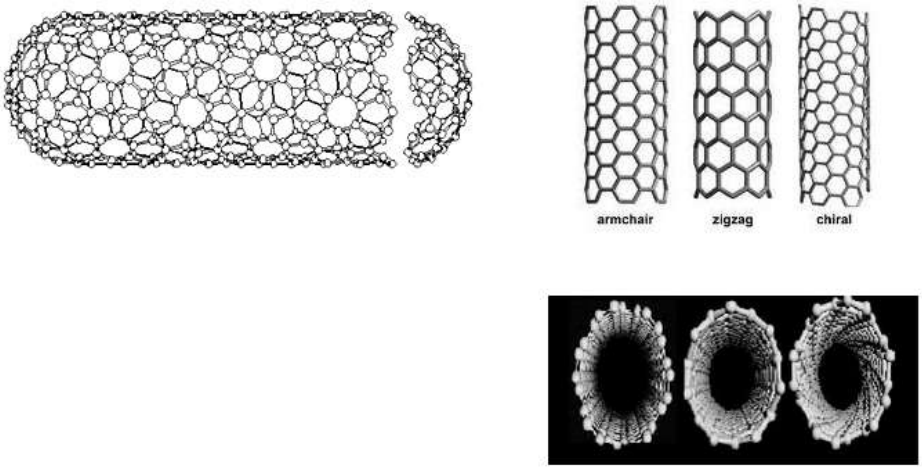

Figure 1.3 SWCNT.

Figure 1.4: MWCNT

Table 1.2 Characteristics of CNT[14]

Tensile strength	63 GPa
young modulus	1.25TPa
Density	1.3 gm/cm^3
Diameters range	1nm-100nm

1.4 PET/CNT nanocomposite

Recent studies have shown that PET have excellently worked as a matrix in which small amount of CNT added in the PET enhances the thermo mechanical and electrical properties [10, 15-17]. Some groups of researchers have studied the improvement in the Properties of PET by different techniques [13-34]. Good dispersion and alignment of CNT in the PET nanocomposite fibers has good impact on improving their properties. Since, CNT are produced in agglomeration form, different techniques needed to separate them, disperse and distribute them in the matrix. Nanocomposite fiber produced with such configuration will have good performance. Today, the two major challenges to any researcher in order to develop high performance PET/CNT nanocomposite fibers are the distribution and the alignment of CNT in the PET matrix. To achieve well aligned, good adhered and uniformly distributed CNT in the PET matrix, the nanocomposite fibers are processed either via in situ polymerization [18] or melt extrusion spinning processes[10].

1.5 Melt Extrusion Spinning

Melt extrusion spinning process is the most simple and economical process. The uniform distribution of CNT in the PET matrix can be obtained by using twin screw extruder with mixing elements in melt extrusion process. In addition, the alignment of CNT in nanocomposite fibers can be accomplished by further melt spinning or drawing process.

Melt extrusion process setup of Twin screw extruder is schematically shown in the Figure 1.5. In order to obtain the different proportion of PET and CNT, two separate computerized control feeders will be used for feeding PET (matrix) and CNT (reinforcement) into the Extruder (barrel). The temperature throughout the barrel will be maintained above the melting point of the matrix. PET/CNT nanocomposite melt will be extruded through the die consisting of 10 holes spinneret as shown in Figure 1.6. The extrudate will be cooled by air flowing perpendicular to the flow of filaments. The solidifying polymers are drawn further by the winders.

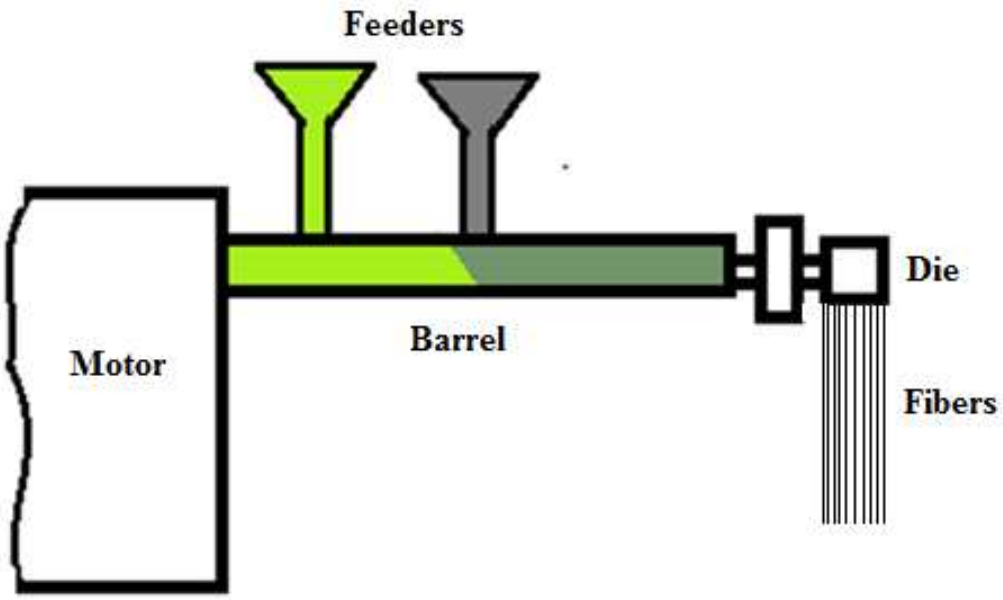

Figure 1.5: Melt extrusion set up

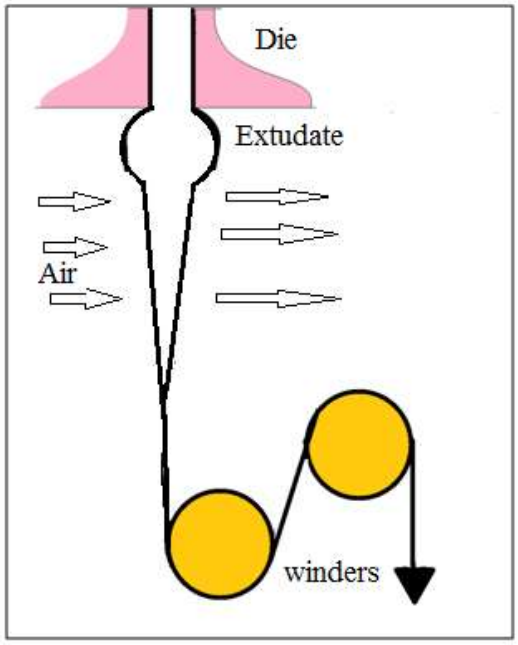

Figure 1.6: Melt-spinning process

1.6 Objectives

The main objective of the present study is to produce high strength PET/CNT nanocomposite fibers using melt spinning process. The study will include the influence of CNT and process parameters on the mechanical properties and processiblity of PET/CNT nanocomposite fibers. In addition, effects of die temperature and spinning speed on the fiber quality will be studied.

1.7 Challenges

1. To obtain good distributed and dispersed CNT into the PET/CNT nanocomposite fibers.
2. To obtain well aligned CNT in the PET/CNT nanocomposite fibers

1.8 Motivation

1. To enhance the mechanical properties of PET material, therefore broaden its applications.

CHAPTER 2

LITERATURE REVIEW

As discussed earlier that Polymers and nanomaterials composites are produced using different techniques like in situ polymerization, solution spinning and melt spinning process. Using these techniques various investigations has taken place. The following sections summarizes those various investigation individually.

2.1 Effect of CNT on PET/CNT nanocomposite

Mazinani et al. [10] have studied the properties of the melt spun PET/MWCNT nanocomposite fibers. A commercial PET/CNT master batch, composed of PET and 15wt% MWCNT was used. Later, this master batch was diluted with PET using melt mixing method to obtained different concentration of MWCNT in PET/CNT nanocomposite fibers. They produced PET/CNT nanocomposite fibers using twin screw extruder. The minimum average diameter possible achieved was 48μm. Furthermore, the study involved the effect of main parameters such as draw ratio (DR) and MWCNT concentration impact on their crystalline nature as well as on mechanical and electrical properties. Five different DR and weight percentages of CNT ranging from 1 to 7% were

studied. The crystallinity as observed from DSC was found to be higher for pure PET fibers when compared to the composite fibers at 3 wt% for three different DRs. For PET the crystallinity increased (from 17.2 to 23.5%) with increasing DR (at 20% DRmax(470) to 60% DRmax (470)). PET was not processable at DRmax. The crystallinity for the composite decreased (from 16.3, 15.4 to 14.7%) with increasing DR (at 20% of DRmax, 60% of DRmax to DRmax). SEM and TEM results showed agglomeration and poor dispersion of CNT in PET matrix. The orientation techniques (Raman and FTIR spectroscopy) showed the presence of highly oriented CNT in PET matrix. In addition, the crystalline characterization (using DSC and XRD) and the orientation techniques displayed a decrease in both the crystalline content and the polymer chain orientation. Further, the tensile properties of spun PET/CNT nanocomposite fibers were not much affected as shown in Figure 2.1. It was observed that, above 3 wt% CNT, the fibers were brittle with lower drawability. Figure 2.2 indicated that three times elongation was possible for PET/CNT nanocomposite fibers containing 1 and 3 wt % CNT while comparing to pure PET fibers. It was documented that increase in the elongation owed to prevail of amorphous phase in PET/CNT nanocomposite fibers.

Furthermore, the modulus of Pure PET and PET/CNT (2wt%) rod like fibers were reported to be 2.3± 0.5 and 2.607±0.2 GPa, respectively. The elongation for pure PET and PET/CNT (7 wt %) fibers were 500 and 4%, repectivley.

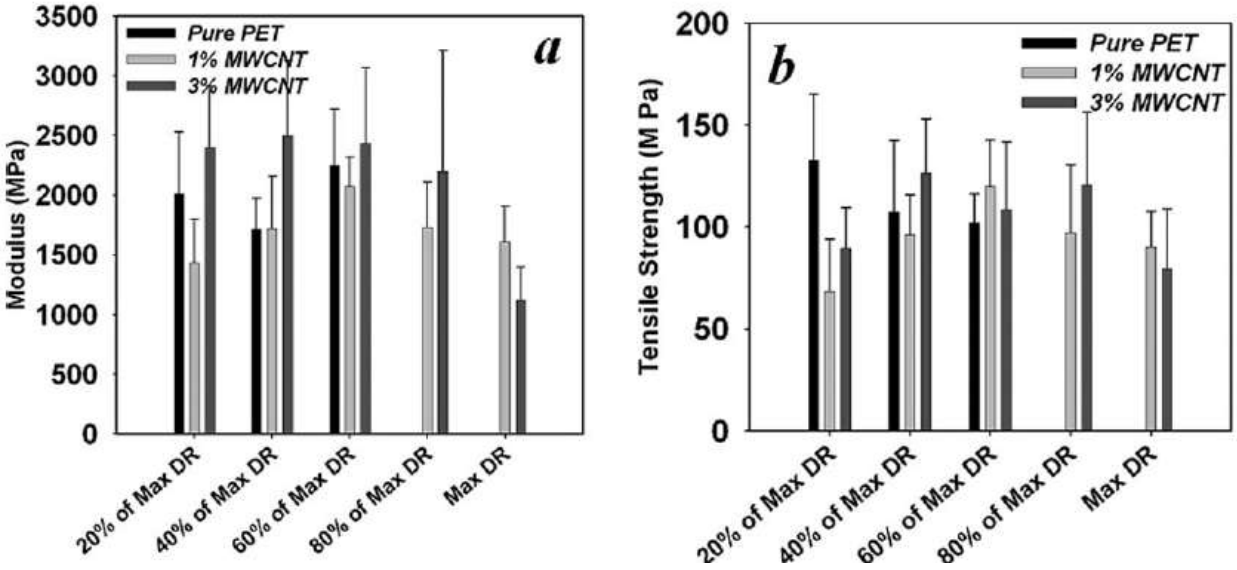

Figure 2.1 Mechanical properties [10].

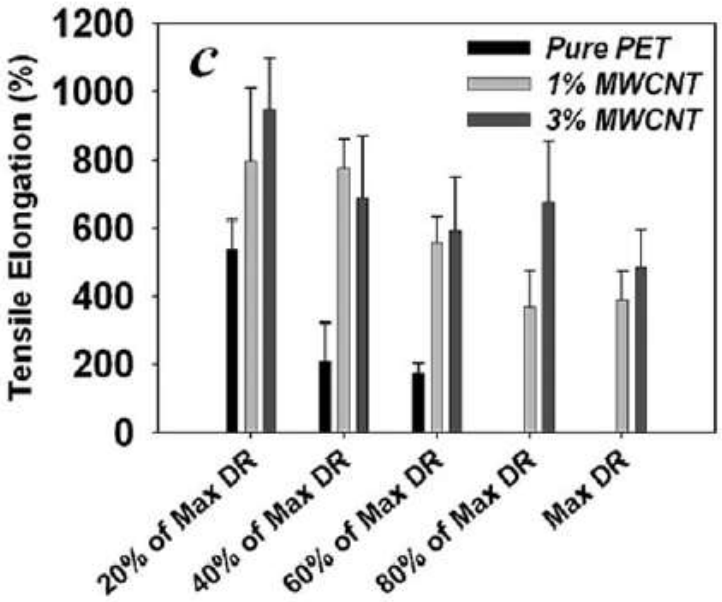

Figure 2.2 Elongation at break [10].

Kim[15] et al studied PET composite reinforced with MWCNT functionalized with carboxylic acid group(MWCNT-COOH). Both PET and MWCNT (prepared by thermal CVD method) were purchased. For functionalizing, a mixture of concentrated HNO3 and H2SO4 in a volumetric ratio of 1:3 was added to CNT and sonicated at 80˚C for 4 hours. The PET nanocomposites were fabricated by melt compounding in twin-screw rheometer with heating zone temperature 270, 280, 285, and 275C, and screw speed of 20 rpm. CNT content studied was 0.1, 0.5, and 1.0 wt%. The extruded composite was cut into pellets with constant diameter and length. FTIR studies of the composite showed possible interactions between the carboxylic acid groups of MWCNT and the ester groups in PET macromolecular chains by hydrogen bonding. Hydrogen bonding was thought to result in good dispersion and enhance interfacial adhesion between MWCNT and PET matrix. DMA studies showed that the storage modulus and loss modulus increased with increasing frequency and MWCNT content. The increase appeared more at lower frequencies.

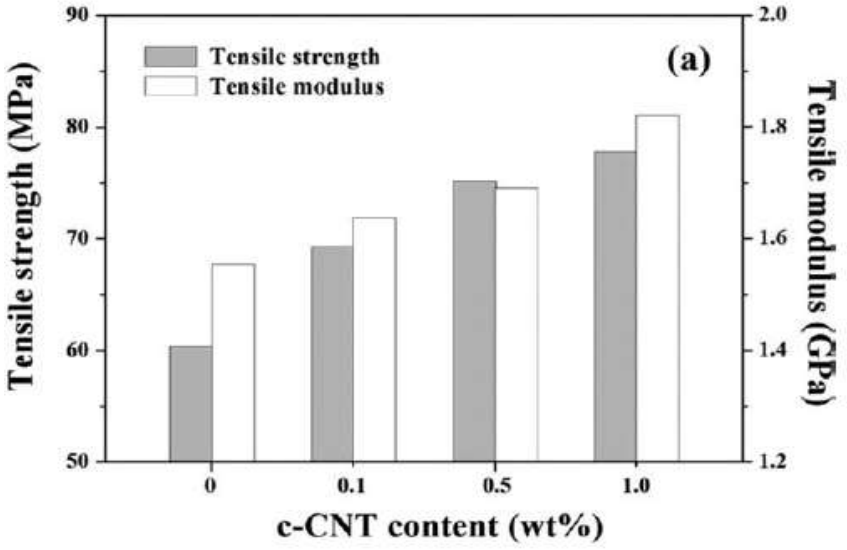

Figure 2.3 Mechanical properties [15]

Tensile studies showed that tensile strength and elastic modulus of the PET nanocomposites increased significantly with increasing the c-CNT content due to the nano reinforcing effect of the c-CNT shown in Figure 2.3. This increase was attributed to the good dispersion and enhanced interfacial adhesion between MWCNT and PET matrix which made the composite more favorable for effective load transfer from the polymer matrix to the nanotubes. This leds to substantial improvement in the tensile properties. The elongation at break however decreased because of the increase in the stiffness of the PET nanocomposites and due to the formation of micro-voids around the nanotubes.

Zhifei et. al. [16] investigated the crystalline and rheology behavior of CNT/PET composite fibers containing CNT concentration 0.5, 2, 4, 8 and 10 wt% and electrical conductive of cloth woven by these composite fibers and common terylene. The

crystallinity was observed to decrease from 41.3% to 30.1% with increasing CNT concentration from 0.5 to 10 wt%. Crystal temperatures increase from 215 to 231℃ with increase in CNT concentrations. This was attributed to the nucleating effect of CNTs. SEM micrographs showed good dispersion of CNTs in PET matrix with a scale of 2 μm for all the CNT concentrations. It was documented that shear thinning effect prevailed as the CNT contents increased in PET matrix. However, at low shear rate it was reported that shear viscosity increased with concentration of CNT. These behaviors with respect to shear rate were observed for CNT concentration above 2wt%. Furthermore it was documented that the viscosity of these composite fibers was even lower than that of pure PET fibers. Since CNT being one dimensional structure possed shear thinning ability like polymer hence at high shear rate it oriented itself to some extend and induced rapid decrease in the viscosity of the composite. Optical Microscope analysis revealed the composite fiber to have an ABA sandwich structure with conductive composite sandwiched between PET matrices. Discontinuity was also observed along the length for the conductive composite layer, which was not desirable for good electrical conductivity. The volume electrical conductivity followed the percolation scaling law with the scaling exponent of 5.5, which was much higher value when compared to other CNT-polymers. The reason behind this increase was not explained. The volume electrical conductivity of CNT/PET composite fiber was 103 Ωcm which was 12 folds lower when compared to pure PET. Cloth of composite fiber and terylene (1:3) had an average charge surface density of 0.25 μC/m2; surface resistivity of 1.2 x 106 Ω.

Rodríguez et al. [19] studied the tensile properties of PET-SWCNT bars (2 X 4 mm^2 and several micrometer length) composite prepared by in-situ polymerization. The samples for tensile test were prepared by injection molding with pressure 70 MPa, melt temperature 260–270°C, mould temperature 30°C, hold time 6s and cool time 20s. Three configurations of composites containing 0.1, 0.2 and 0.3 wt% SWCNT in plain PET were tensile tested using electro mechanical tensile machine. It was observed that the elastic modulus (2.6GPa) and yield strength (58.2MPa) of nanocomposite bars increased by 6.5, and 11.9 % with an addition of 0.3wt% SWCNT. However, the failure strain decreased by 89.1%.

Wang[20] et al studied influence of reinforcement of a low content (0.01 to 0.2 wt %) of purified and functionalized MWCNT-COOH on morphology, crystallization and dynamic mechanical properties of in PET/CNT nano composite. The MWCNTs were purified and functionalized the composite was prepared by in-situ polymerization method. The increase in CNT content hindered the dispersion but it also led to more interaction between the filler and the matrix. It was documented that increase in crystallization temperature was observed owing CNT concentration from 194.3 °C for PET and 200.6, 202.9, 203.3, and 203.88 °C for composites with 0.01, 0.05, 0.1, and 0.2 wt %, MWCNTs, respectively. This was attributed to the nucleating effect of CNT. With further increase in CNT content, the nucleating efficiency decreased although the crystallization temperature was increases. This was attributed to the restriction on chain mobility leading to the formation of imperfect crystallites along with perfect crystals.

This was associated with the observation of double melting peaks in the DSC melting curves. Dynamic mechanical analysis (DMA) were done by a three-point bending test in a temperature range of 45 to 100 °C with the rate of 3°C/min, frequency of 1 Hz and amplitude of 0.01mm. The storage modulus increased from 266 MPa for plain PET to 328 MPa for 0.05 wt % MWCNT composite. When the CNT content was increased to 0.1 and 0.2 wt %, the storage modulus was decreased dramatically, even lower than that of plain PET (290 MPa for 0.1 wt % and 220 MPa for 0.2 wt %). Improvement in storage modulus at low content was attributed to the good dispersion MWNTs and the formation of MWNTs network throughout the matrix. The higher content led to poor dispersion of, restriction on mobility of PET chains and formation of imperfect or smaller/thinner crystallites, which led to the decrease in storage modulus.

Anand[17] et al, studied the crystallization behavior of poly(ethylene terephthalate) (PET) and SWCNT (1.4 nm in diameter, 2–5 μm in length and purity of 50–70%) composites at concentrations of 0–3 wt%. Both PET (in pellets form) and SWCNT (Prepared by arch discharge method) are purchased. The PET nanocomposites were fabricated by melt compounding in a laboratory scale kneader operating at 40 rpm for 4 min at 270°C with CNT content of 0.0, 0.03, 0.1, 0.3, 1.0 and 3.0 wt%. DSC studies showed the increase in crystallization temperature with SWNT content. With the addition of lowest content of CNT of 0.03 wt%, crystallization temperature increased by 10°C. With further increase in content, the Tc values continue to increase but at a slower rate. With the increase in content from 0.03 to 0.3wt% the Tc increased by only about 10°C.

This is attributed to the saturation of the nucleation effect, resulting in reduced dependence on the SWNT induced nucleation, possibly because of the large surface area and good dispersion of SWNT. The melting temperature and enthalpies however remained unaffected by the addition of SWNT. Wide-angle X-ray diffraction (WAXD) experiments were performed to study crystalline orientation in the composite. Macroscopic orientation of neat PET and the composite was created by stretching the samples under mechanical stress. This was done by compression molding and stretching the samples while heating in contact with a stainless steel plate at 150°C. WAXD pattern showed crystalline orientation in both neat PET and composite. These oriented samples are then heated in hot-stage to the melting temperature and then cooled to recrystallize. WAXD patterns of the resulting nanocomposite and neat PET indicated that the composite sample showed oriented crystallization along the original stretching direction, while crystalline orientation was random in the neat PET. It was concluded that crystalline orientation in the sample was a result of the oriented SWNT acting as nucleating sites for the reorientation of the crystallizing PET molecules.

Yao Gao [21] et al studied non-isothermal crystallization behavior of functionalized MWCNT (f-MWCNT) and PET composite. The MWCNT were functionalized with HNO3 and maleic anhydride. Different compositions of PET and pure MWCNT or f-MWCNTs (0.1, 0.5, 1.0 and 2.0wt % were melt blended through using a twin-screw extruder with set temperatures of 230–265°C from hopper to die. SEM studies showed that the Pristine MWCNTs are mainly aggregated due to the Vander Waal's forces

among MWCNTs. whereas functionalized-MWCNTs showed good dispersion because it was shortened by its length due to oxidization reaction with HNO3. Miscibility and interfacial interaction between PET and functionalized-MWCNTs was greatly improved, possibly due to the hydrogen bond effect between PET chains and f-MWCNTs. It was investigated that glass transition temperature and cold-crystallization peak temperature decreased with f-MWCNT content. However, melt-crystallization peak temperature of PET increased with increasing f-MWCNT content. The increase in the crystallization rate (effect on crystallization peak temperatures) was attributed to enhancement of chain segments mobility, and to the nucleation effect of f-MWCNTs, which induced crystallization on the surface of the f-MWCNTs.

Mun et al.[18] have produced the hybrid PET fibers compose of PET with 0.4 to 1.5wt% functionalized MWCNTs, via capillary die using in situ polymerization technique. They have studied the enhancement in the mechanical properties of the PET fibers with small addition of functionalized MWNTs compare to pure PET. Ultimate tensile strength improved from 46MPa of pure PET to 60MPa of hybrid PET with 1.0wt% modified MWCNT and to 57MPa with 1.5 wt% modified MWCNT. The decrease in the ultimate tensile strength at higher CNT loading was due to agglomeration effect of CNT in PET matrix. On the other hand, It was observed that with increasing draw ratio (DR) from 1 to16, unlike the other [22], decrease in the tensile strength was observed. For instance, for PET/modified CNT nanocomposite fiber with 0.3wt% content, DR of 16 has a tensile strength of 44 MPa, whereas the same composition of CNT nanocomposite with DR 1

has a tensile strength of 57Ma. This decrease in the ultimate strength was due to the de-bonding around the PET–MWCNT interfaces and void formation because of extra stretch during spinning. This similar effect was reported for PET/modified CNT nanocomposite fibers containing 0.5, 1.0 and 1.5wt%.

2.2 Effect of CNT on other Polymers

A group of researchers, Jun Young et al. (2007) [23] investigated the crystallization behaviors and mechanical properties of Poly (ethylene 2,6 naphthalate) (PEN) /MWCNT nanocomposite. These nanocomposites were produced by using twin screw extruder (intermeshing co-rotating). They reported that incorporation of CNT in PEN matrix has increased the crystallization rate of PEN/CNT nanocomposite. It was reported that inclusion of CNT on PEN matrix increased the mechanical properties such as tensile strength and modulus. Tensile strength of PEN/CNT improved to 32% (90MPa) compared to pure PEN (68MPa). Likewise, it was also reported that incorporation of low content MWCNT (Multi wall carbon nano tube) improved the modulus from 1.65 to 1.75GPa that was in good agreement with theoretical value. However, compared to theoretical values larger deviation was reported with higher concentration of CNT. The reason for decreasing in mechanical properties was attributed to the increase in CNT content. As explained elsewhere [24], the CNT tended to agglomerate due to intrinsic van der Waal's attraction between the nanotubes, hence hindered the efficient load transfer to polymer matrix.

Carine et al. (2009) [22] investigated the influence of spinning conditions on the structure and properties of polyamide(PA)-12/MWCNT nanocomposite fibers. The study incorporated 3 and 7wt% of CNT in the PA-12 matrix. The authors reported that the increase in draw ratio has increased the degree of alignment of molecular chain PA-12 and CNT. In addition, incorporation of CNT in PA-12 has increased the modulus by 75% (from 0.9 to 1.7MPa), but breaking strength and failure strain was reduced. However, impact of draw ratio on individual pure PA-12 and PA-12 /CNT (7 wt %) fibers has significant improvement in the mechanical properties. It was reported that a draw ratio of 7 enhanced the modulus and break strength of plain PA-12 by about 270% (from0.9 to 3.3GPa) and 260% (from118 to 422MPa), respectively. On the other hand, draw ratio of 7 enhanced the modulus and break strength of PA-12/CNT (7 wt %) by about 200% (from1.7 to 5.1GPa) and 230% (from117 to 389 MPa), respectively. However, elongation at break dropped from 330 to 19 % and 146 to 10 % for pure PA-12 and PA-12 /CNT (7 wt %) nano composite fibers, respectively.

Kwiatkowska [25] et al. studied in-situ polymerization of polybutylene (PBT)/CNT composite containing different type of 0.2 wt % CNT. Three different kinds of carbon nanotubes were used such as plain MWCNT functionalized MWCNT- NH2 and oxidized SWCNT(oSWCNT). Thermal analysis of PBT/CNT showed a clear shift of exothermal peak towards higher temperatures of 12 to 17 °C compare to pure PBT. In addition, there was no influence on the melting points of the composites. The crystallinity was higher for MWCNT and MWCNT- NH2 and there was no change in the crystallinity of oxidized-

SWCNT composites compared to pure PBT. Moreover, maximum crystallinity was obtained for composite containing functionalized MWCNT. This effect was due to interaction of CNT-polymer matrix in which CNT acted as a nucleating agent. The study of dynamic behavior on PBT/CNT composite showed the increment in the storage modulus, under the glass transition temperature, due to an addition of oSWCNT and MWCNT. This was attributed to the variations of molecular mobility of polymer chains and stiffening effect of CNT. It was also documented that a homogeneous distribution of CNT with agglomeration at some places was observed. Static tensile tests showed that both MWCNT and MWCNT-NH2 composites had little influence on the elastic modulus but there was a slight increase in the tensile strength as shown in Figure 2.4 In contrast, the oxidized-SWCNT has shown a clear increase in elastic modulus and a slight decrease in tensile strength.

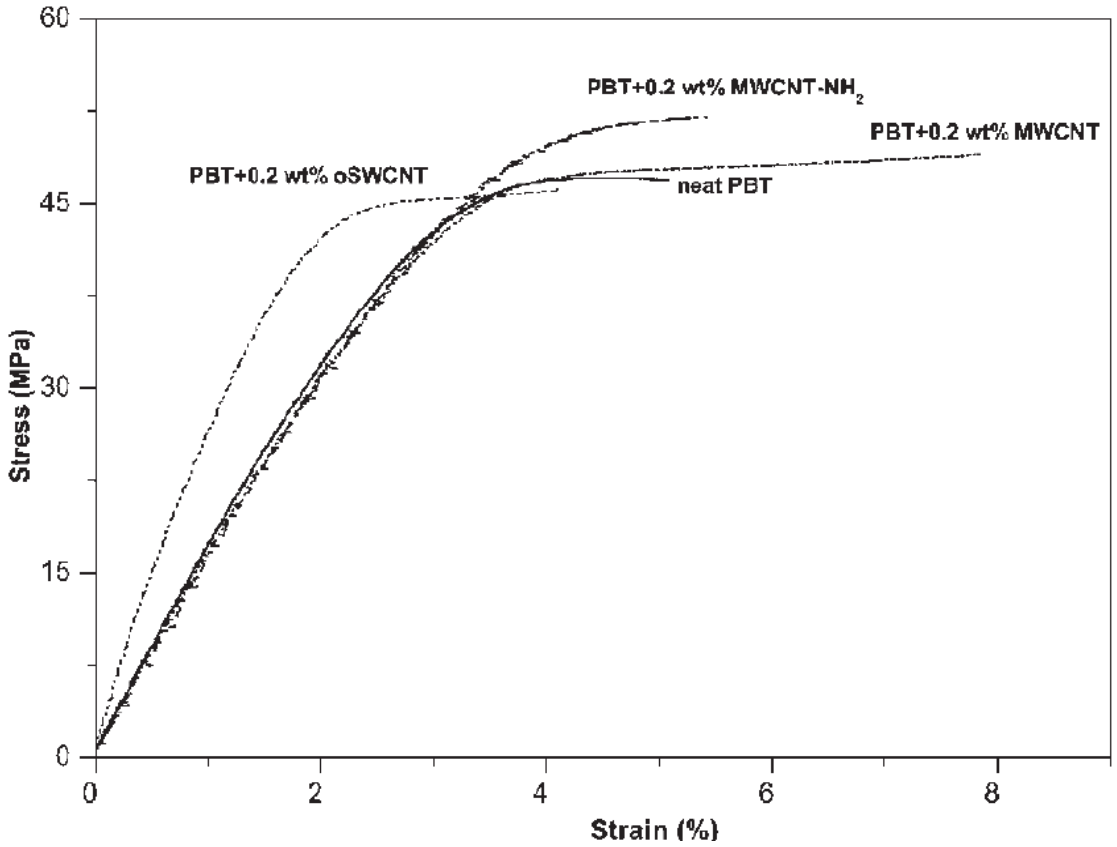

Figure 2.4 PBT/CNT stress strain Curves [25]

Edgar et al. (2004) [26] manufactured a poly vinyl alcohol (PVA) /CNT Composite fiber of 50 µm diameter from a 0.4 wt % Single Wall Carbon nanotubes (SWNT) with surfactant (Lithium dedocyl sulfate) reinforced the poly vinyl alcohol (PVA) using coagulation technique. It was reported that it could be drawn to five time its initial length. It was found that ultimate modulus strength is twice the pristine PVA (80GPa) and tensile strength eight times the Pure PVA material (230MPa).

Mikolajczyk et al. (2010) [27] have manufactured of polyacrylonitrile (PAN) /CNT nanocomposite fibers. The polymer polyacrylonitrile (PAN) was used as a matrix reinforced with different types of CNTs (1 wt %) such as short, long and modified MWCNT (length: 1000-2000, 10000-30000 and 300-2000nm, respectively: Averaged diameter 10-30, 10-20 and 5-20nm, respectively), and SWCNT (30nm-50nm, diameter 2nm-3nm). PAN with Short & long CNTs was spun using wet spinning process through multistage drawing. It was documented that adding of CNT brought a little increment in the tensile strength about 5 to 12% in pure PAN of 510MPa. However, young's modulus has significant increment from 28 to 56% over 7.8GPa. It was noticed that polymer composite with both short and modified MWCNT has maximum tensile strength of 570MPa each.

S.kumar et al. [28] have reported 16% increment in the tensile strength and 54% increment in the modulus of PP/5wt% carbon nanocomposite spun fibers. The strength of pure PP was reported to be 490MPa and improved to 570MPa with an addition of 5 wt % CNT. This increment was due to alignment and distribution of carbon fiber in polymer matrix.

Polymer composites are used in variety of industrial and household applications. Efforts are being made to increase the range of applications of polymer composites by modifying with organic and inorganic nanomaterials such as carbon nanotubes, carbon nanofibers, nanoclay, nanosilica and other nanomaterials. The blending of these organic and inorganic nanomaterials in polymeric matrix is not an easy task. The major hurdle in

preparing these blends is the agglomeration of nanoparticles within the matrix. It is very important to consider an effective mixing method to have a good dispersion of these nanomaterials within the polymer matrix. Several methods have been tried in literature to achieve effective mixing using different techniques.

Recent studies have shown that PET have excellently worked as a matrix in which small added amount of CNT enhanced the thermo-mechanical and electrical properties. Some of the recent studies are summarized in the Table 2.1. Some groups of researchers have studied the improvement in the Properties of PET by adding CNT through different techniques such as solution spinning or in situ polymerization process. The CNT used in those studies was modified with acid or functional group and the final product was nanocomposite. Moreover, the studies were about the effect of modified CNT on the crystallization, rheological and electrical properties of the PET/m-CNT nanocomposite. Some other group of researchers has produced the PET/CNT nanocomposite fibers using commercialized PET/CNT masterbatch. The minimum reported diameter of those fibers was 48μm. In addition, the studies were limited to the higher concentration and also achieved very little improvement in the mechanical properties due to CNT agglomeration. Therefore, the present work studied the effect of CNT on the PET/CNT nanocomposite fibers using melt extrusion spinning process technique. The study also includes the investigation of the effect of CNT concentration from 0.1wt% to 7.5wt% CNT on the quality of the spun PET/CNT nanocomposite fibers.

Table 2.1 Literature review

Polymer (Matrix)	Nanomaterials (reinforcement)	Improvement in Tensile Strength	Improvement in Modulus	Group of Researchers
PET (Fibers)	Functionalized CNT (1wt %)	30%(60 MPa)	31%(2.89GPa)	Mun et al. (2008)
PET(Fibers)	MWCNT (3wt %)	20%(120MPa)	12% (2.61GPa)	Mazinani et al (2010)
PET(Bulk)	Modified CNT (1wt %)	29% (77.8MPa).	17% (1.82GPa)	Young Kim et al.(2010)
PET(Bars)	SWCNT (0.3 wt %)	11.9% (yield strength 62 MPa)	11.9% (2.9GPa)	Rodriguez et.al(2010)
PP(Fibers)	CNF (5wt %)	54% (570MPa)	16% (7.1GPa)	S.kumar et al.
Polyamide 12(Fibers)	CNT (7 wt %)	pure PA12 (422 MPa)and PA12/CNT (389MPa)	54.4%(5.1GPa)	Carine et al.(2009)
Polyacrylonitrile(Fibers)	CNT (1 wt %)	12% (570 MPa)	56wt% (12.18 GPa)	Mikolajczyk (2010)
poly(ethylene 2,6-naphthalate)(bulk)	MWCNT	24% (82MPa)	13.6 % (1.75GPa)	Jun Young et al. (2007)

CHAPTER 3

EXPERIMENTAL

This chapter includes the individual characteristics of PET and CNT material. It also describes the method for blending these two materials together and describes the melt extrusion and spinning process parameters for the production of PET/CNT nanocomposite fibers. In addition, this chapter describes the characterization techniques that are used to measure the mechanical properties and the quality of the PET/CNT nanocomposite fibers.

3.1 Experimental Procedure

3.1.1 Poly (ethylene terephthalate) Material

A Commercial grade Poly (ethylene terephthalate) (PET) material (grade: BC-112) supplied by SABIC was used for fiber production. The properties of PET, as indicated by the supplier, are the intrinsic viscosity, 0.84 dl/g, and bulk density, 838 kg/m3.

3.1.2 CNT Material

Aligned Multi-wall Carbon nanotubes (MWCNTs) (Figure 3.1) were produced at KFUPM using chemical vapour deposition (CVD) process. Ferrocene was used as the source of iron catalyst and xylene was used as hydrocarbon source. Ferrocene was

dissolved in xylene. Argon (Ar) gas was flown into the reactor to flush any traces of oxygen while raising the temperature to the set point. After the temperature had reached the desired condition, the hydrocarbon liquid with ferrocene catalyst was injected into the first reaction chamber a rate of 20 ml/min with 2000 ml/min hydrogen gas. The amount of catalyst loading was fixed at 1 wt%. The total reaction time is set to one hour at the temperature of 800 °C. The total yield of CNT obtained was about 2 g/run.

3.1.3 CNT heat treatment

A Lindberg/Blue furnace was used for CNT heat treatment as shown in Figure 3.2. The CNT materials produced were heat treated in the furnace at 375 °C for the duration of 24 hours.

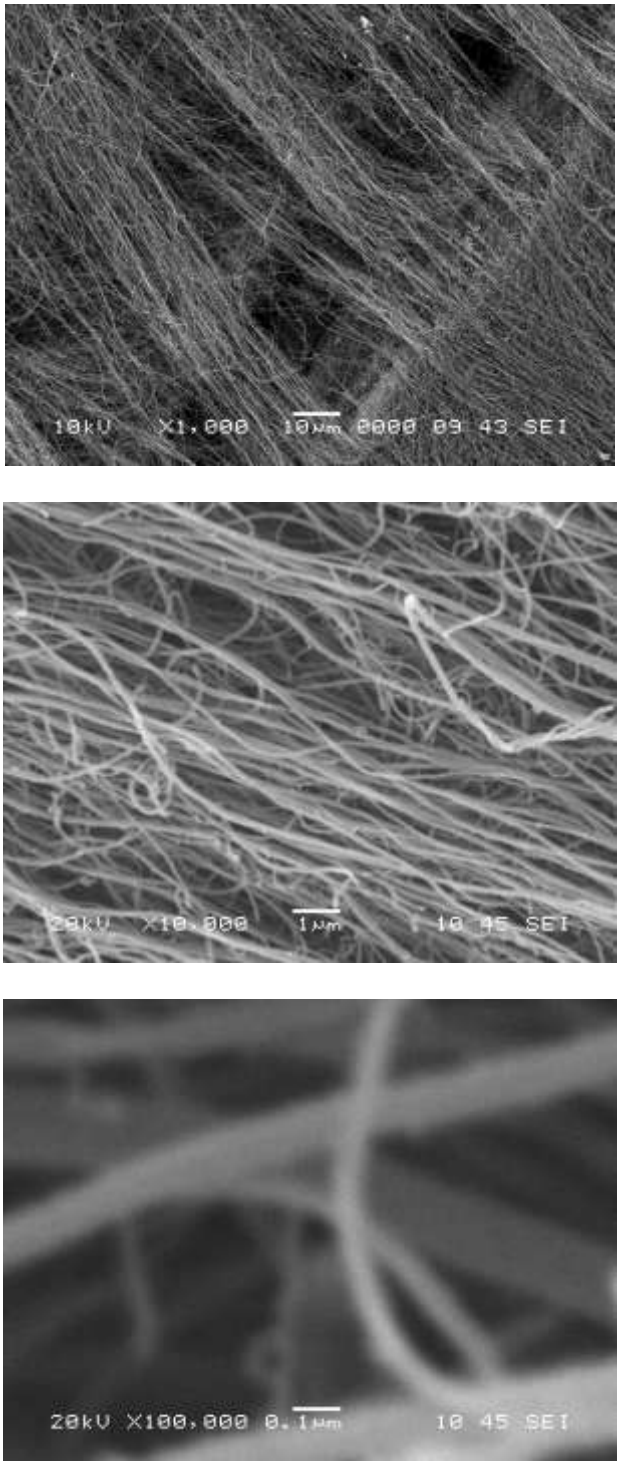

Figure 3.1 SEM micrographs of aligned MWCNT's.

3.1.4 Moisture removal

PET is moisture sensitive; therefore, prior each extrusion run the moisture has to be removed from the extruded material. Before any extrusion process, PET pellets and CNT materials were vacuum dried in a vacuum oven of SheLab as shown in Figure 3.3. The pellets and the CNTs were heated to the temperature of 120 °C for a minimum duration of 10 hours under vacuum.

Figure 3.2 Furnace for heat treatment of CNT.

Figure 3.3 Vacuum oven for drying PET pellets and CNT materials.

3.1.5 Extrusion and Melt Spinning Process

A Thermo Haake® twin screw extruder as shown in Figure 3.4 was used to produce the nanocomposite fibers. This extruder was designed with an L/D ratio of 40. All the heating zones and the screw speeds were externally controlled with a computer. The temperatures of the melt were measured using thermocouple sensors and the pressure at the extruder exit was measured with a pressure sensor. The torque required to turn the screw was electronically displayed and recorded on the computer. The pellets were fed into the extruder barrel through a metered feeder at a constant mass flow rate. The extruder

screws were driven by a motor and its speed can be changed as desired. The pellets melted in the extruder and then the melt was pushed through an adaptor die located at the exit of the extruder. The melt then was flown through a melt pump to the ten-hole spinneret (die) at a constant mass flow rate of 3.5 g/min. The hole diameter was 0.75 mm. The fibers were cooled with the ambient air. The fibers were then spooled onto a drum using a motor winder. The winder was designed and fabricated locally at KFUPM laboratory. The twin screw extruder had seven controllable heating zones and three mixing zones with mixing elements. The material feeding was achieved with the help of a computer controlled feeder. If the required torque reaches the limit, the motor gets tripped off and immediately the extruder shuts down. A temperature profile between 270°C - 290°C was selected by considering the processability, polymer degradation and the equipment limitations. The melt pump speed was set at 3 rpm and the temperature was set at 280 °C to pump the material to the spinneret die. An extruder screw speed of 20 rpm was used and a pressure of 14 to 46 bar was maintained at the extruder die exit.

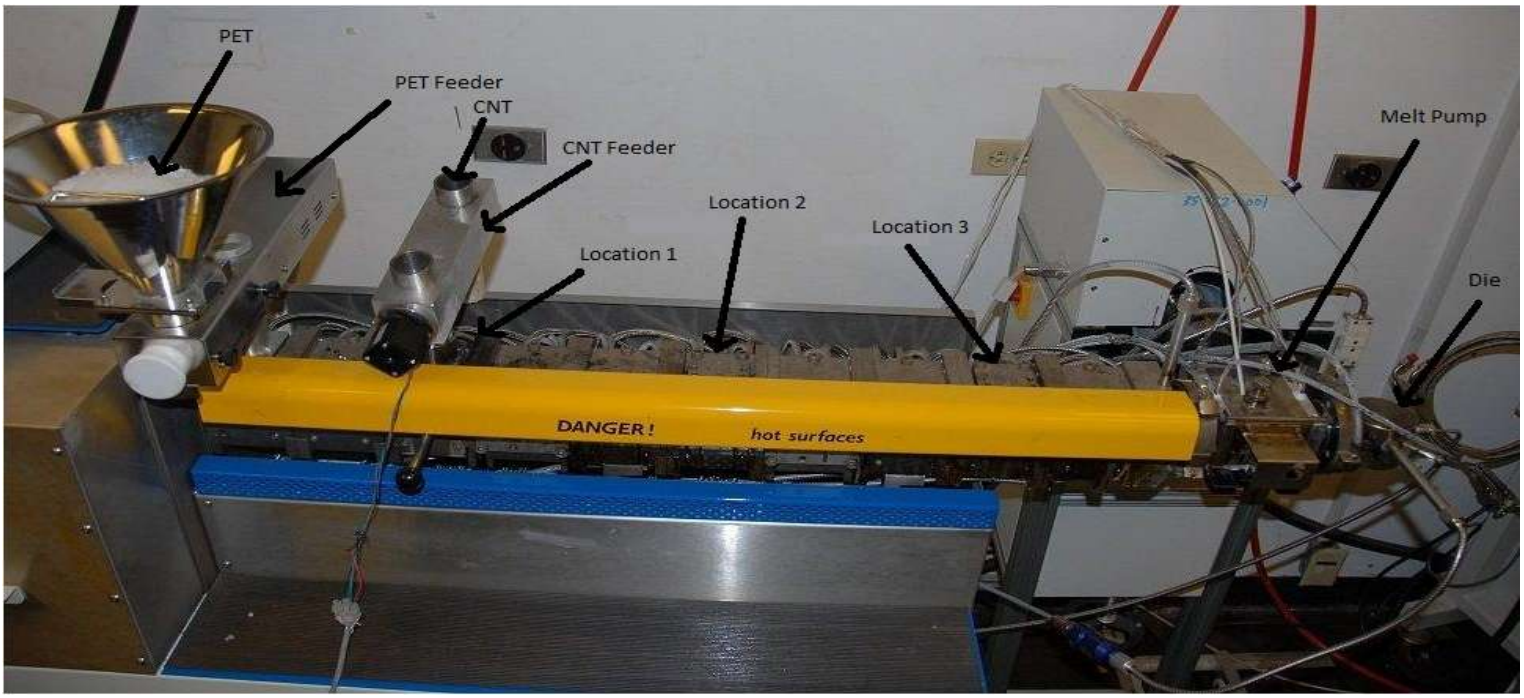

Figure 3.4 Second feeder for blending.

For blending the CNT with PET, a separate feeder was used in addition to the previous one as shown in Figure 3.4. The designing and manufacturing of the second feeder was carried out at KFUPM labs. The feeder was externally controlled using a computer. The PET pellets were fed through the first feeder. The CNTs were simultaneously fed into the extruder barrel from the second feeder. This kind of blending using separate feeders for PET and CNT will give a better control on the homogeneity of the blend when compared to manual mixing of the material and feeding through a single feeder. The feed rates were controlled and calibrated so as to obtain the CNT/PET blend ratios of 0.1, 0.5, 1, 2.7, 3

and 7.5 wt%. The fiber extrudate from the spinneret was later spooled on the winding drum and was spun at different speeds using the winder.

3.2 Characterization Techniques

3.2.1 Fiber Diameter Measurements

Carl Zeiss® optical microscope shown in Figure 3.5 was used to measure the diameter of the nanocomposite fibers. The microscope was set in dark field transmission mode. A small length of the fiber was prepared and placed between two glass plates. This assembly was then placed between the polarizer and the analyzer. The fiber was focused and its diameter was measured using a software, interfaced with the live microscopic image on the computer.

Figure 3.5 Optical Microscope.

3.2.2 Thermogravimetry Differential Scanning Calorimetry (TG-DSC)

TG-DSC test was carried out on the polymer nanocomposite fibers using TA-SDT® instrument shown in Figure 3.6. The CNT weight percent in the nanocomposite fiber was confirmed using the TG-DSC experiments. Samples were prepared by cutting small lengths from the fiber to fit into the alumina pans. Sample weight, in the vicinity of 4.5 mg, was measured with an accuracy of 0.1 µg. All samples were scanned from 40 °C to 1000 °C with a heating rate of 10 °C/min. All experiments were performed under inert environment of Nitrogen gas with a flow rate of 100 ml/min.

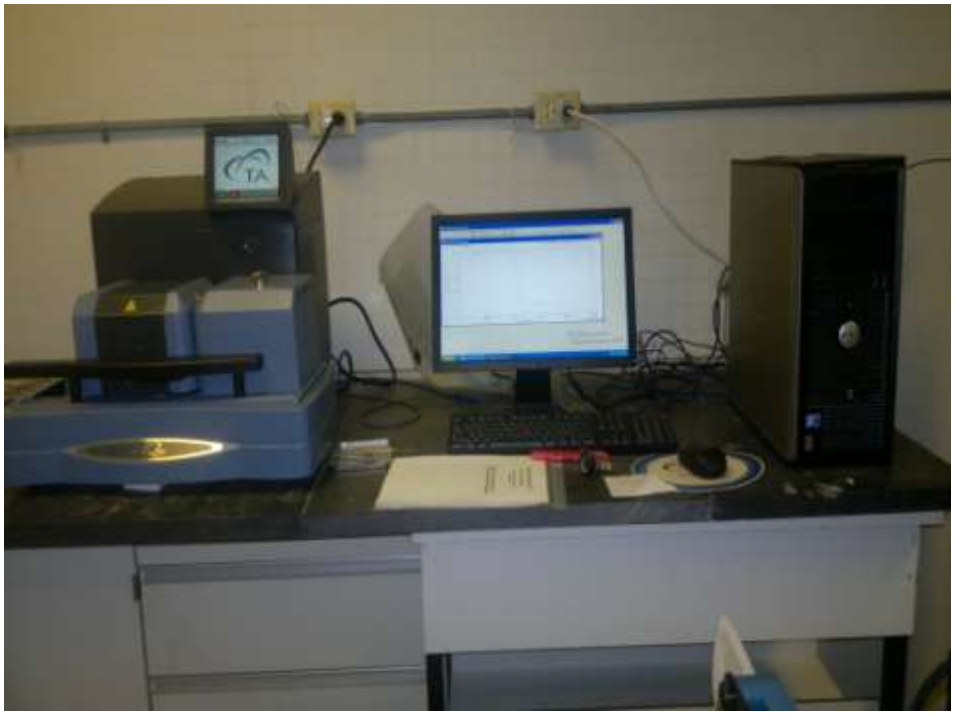

Figure 3.6 TG- DSC instrument.

3.2.3 Scanning Electron Microscopy (SEM)

JEOL® 6400 Scanning Electron Microscope shown in Figure 3.7 was used to study the size and quality of the CNT's produced in the laboratory. It was also used to study the fracture surface of the PET/CNT fibers. Samples were gold coated using a sputtering instrument.

3.2.4 Mechanical Testing

Lloyds® tensile testing machine shown in Figure 3.8 was used for testing fibers in tension. Specimens of nanocomposite fibers were cut to a gauge length of 25 mm and their diameter was measured using the optical microscope. These specimens were then placed on a paper window frame. The fibers were stretched at a controlled rate of 50 mm/min. A load cell of 20 N was used for the tensile tests. The tensile properties such as the yield stress, ultimate tensile strength, modulus and toughness were determined from the tensile test plots. The toughness was calculated as the area under stress-strain curve. Five samples were tested at each condition and the average values of the properties were reported.

Figure 3.7 SEM.

Figure 3.8. Lloyd tensile testing machine.

3.2.5 Work Plan

The melt spinning process involved many process parameters, which have been optimized for good quality products. Effects of CNT distribution in PET matrix, melt temperature, spinning speed, and CNT concentration were studied in the present research work. The sequence and major components of the current work were summarized in the flowchart (Figure 3.9). The entire work was divided into three stages, with each stage addressing the influence of an individual process parameter. In the first stage, the effect of melt spinning temperature was studied by varying the die temperature. Three different die temperatures of 265 ºC, 280 ºC and 290 ºC were considered. The die temperature with the best mechanical properties and spinnability was selected for the remaining research work. In the second stage, the effect of spinning speed on the nanocomposite fibers quality was analysed. In the third stage, the effect of CNT concentration on the mechanical properties of the extruded and the melt spun nanocomposite fibers was studied. Six different CNT concentrations varying from 0.1 % to 7.5 % were considered. The PET/CNT nanocomposite fibers with 0.1, 0.5, 1, 2.7, 3 and 7.5 wt% of CNT were produced and studied.

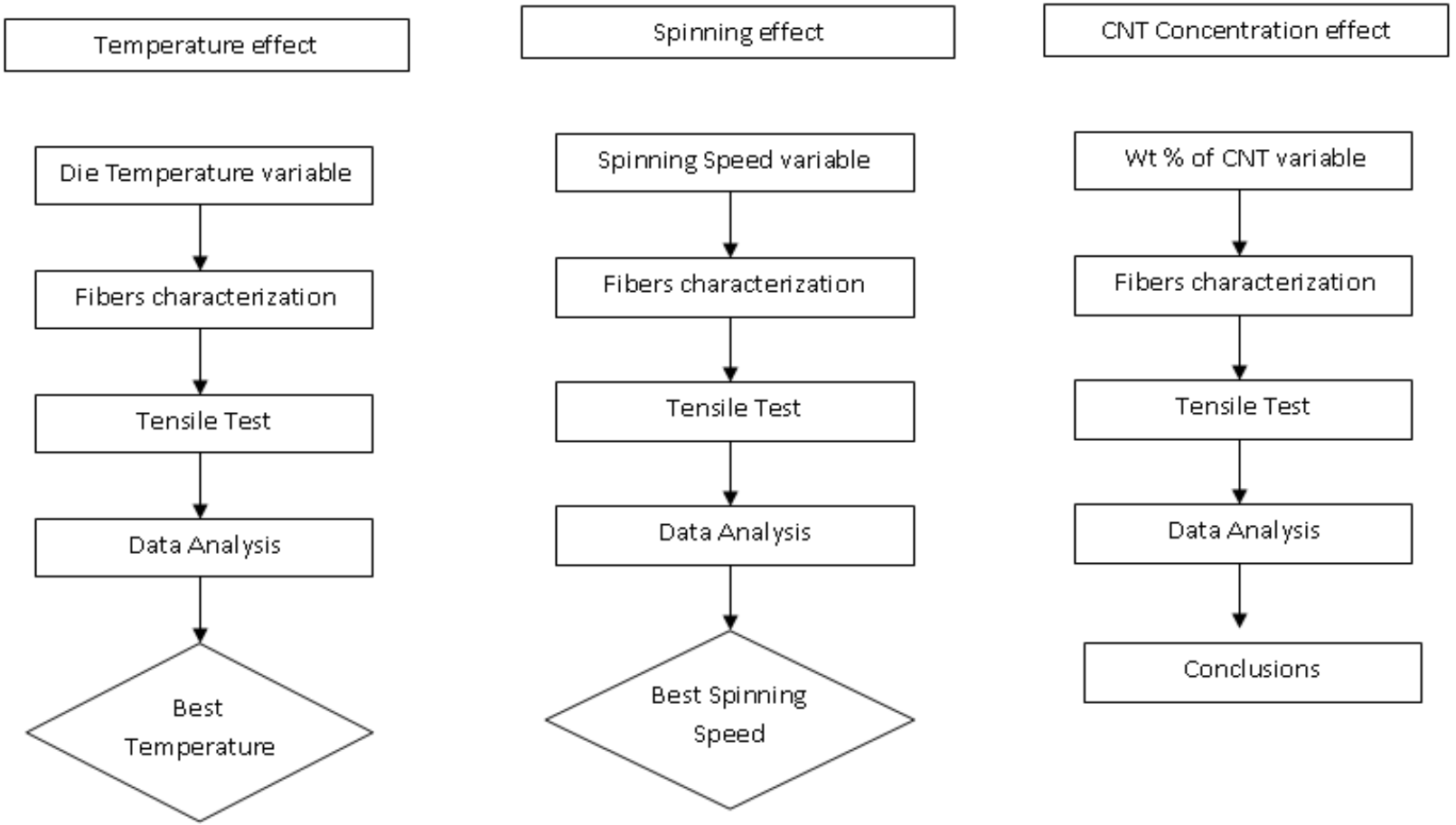

Figure 3.9 Work plan

CHAPTER 4

RESULTS AND DISCUSSION

This chapter consists of four sections. In each section, different process parameters were used for the study and the results obtained are presented and discussed.

4.1 Effect of Die Temperature on Mechanical Properties of PET/CNT Nanocomposite Fibers

Die temperature is one of the factors that affect the processability of polymer fibers. The present study investigates the influence of different die temperatures on the processability, mechanical properties and the distribution and alignment of CNT in PET/CNT nanocomposite fibers containing 1wt% CNT. In this study, the CNT feeder was fixed at position 1 and the extruder temperature profile was fixed at 290 to 275 ˚C, from hopper to last zone of extruder. The PET/CNT fibers were extruded at different die temperatures of 265 ˚C, 280 ˚C and 290 ˚C. The distribution and alignment of CNT in the PET matrix was observed using SEM and the effect of die temperature on the mechanical properties was evaluated using tensile tests. Fibers extruded at different die temperatures were spun using a winder to evaluate the effect of die temperature on spinnability.

4.1.1 SEM Analysis

Figure 4.1 to Figure 4.3 show the SEM micrographs of PET/CNT nanocomposite fibers produced with die temperatures of 265ºC, 280ºC and 290ºC, respectively. A good distribution of CNT was observed for all die temperatures, 265ºC (Figure 4.1), 280ºC (Figure 4.2) and 290ºC (Figure 4.3). As expected, it can be concluded that the extrusion temperature in the range of 265 ºC to 290 ºC does not have an effect on the distribution of CNTs inside PET matrix.

4.1.2 Mechanical Properties

Effect of die temperature on mechanical properties of as extruded PET/CNT nanocomposite fibers was studied. Different mechanical properties PET/CNT nanocomposite fibers are plotted against the die temperatures and presented in Figure 4.4. It can be observed that the die temperature has little effect on the mechanical properties of as extruded PET/CNT (1wt %) nanocomposite fibers which was expected as the die temperatures would not affect the distribution of CNT in the fiber as the CNT has already been mixed in the PET matrix before reaching the extrusion die. However, a good variation in the modulus of elasticity of as-extruded PET/CNT nanocomposite fibers was observed. The fibers obtained at die temperature 290˚C showed high modulus in contrast to the other die temperatures as shown in Figure 4.5. The average value of modulus of elasticity of fiber extruded at 290˚C is 2.1 GPa which is 27% and 20% higher than the values obtained for die temperatures 265 and 280˚C with an average modulus of 1.65 GPa and 1.75 GPa respectively. This improvement is due to the alignment of CNT in the polymer nanocomposite [18, 29]. During the extrusion process, the nanocomposite melt flowed more easily through the

die at 290˚C compared to the die temperatures of 265 and 280˚C which results in decreasing viscosity with increased die temperature, that helps in aligning of CNT and molecular chain of PET/CNT nanocomposite.

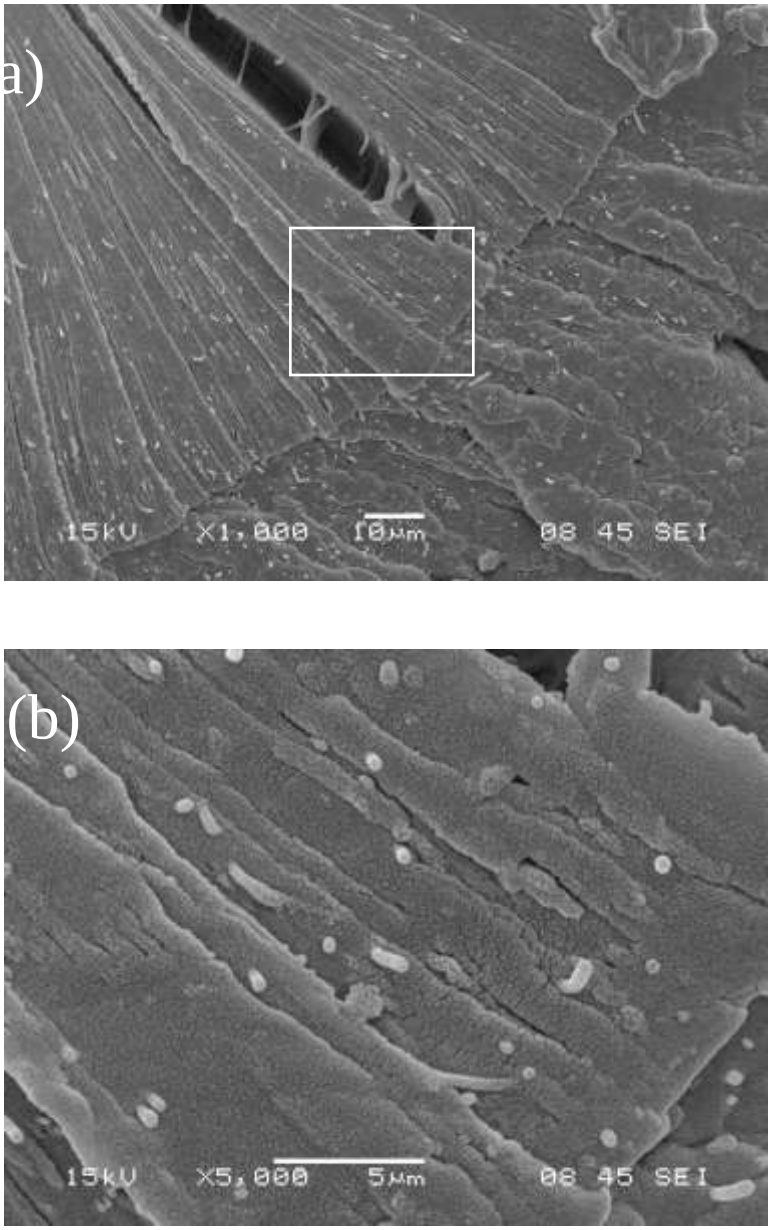

Figure 4.1 Distribution of 1wt% CNT in PETmatrix of PET/CNT nanocomposite fibers at die temperature 265ºC obtained at (a) lower and (b) higher magnifications.

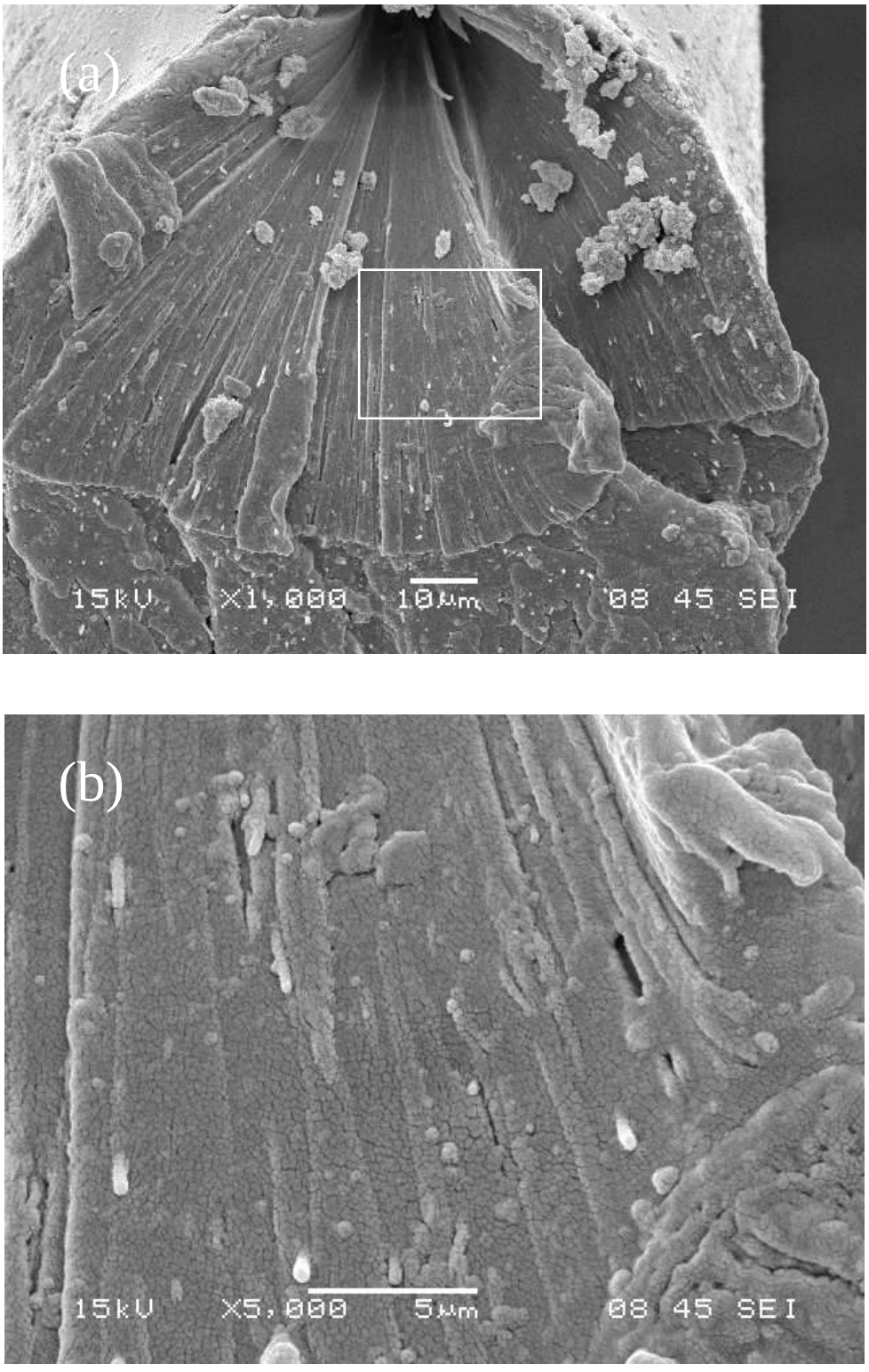

Figure 4.2 Distribution of 1wt% CNT in PETmatrix of PET/CNT nanocomposite fibers at die temperature 280ºC at (a) lower and (b) higher magnifications.

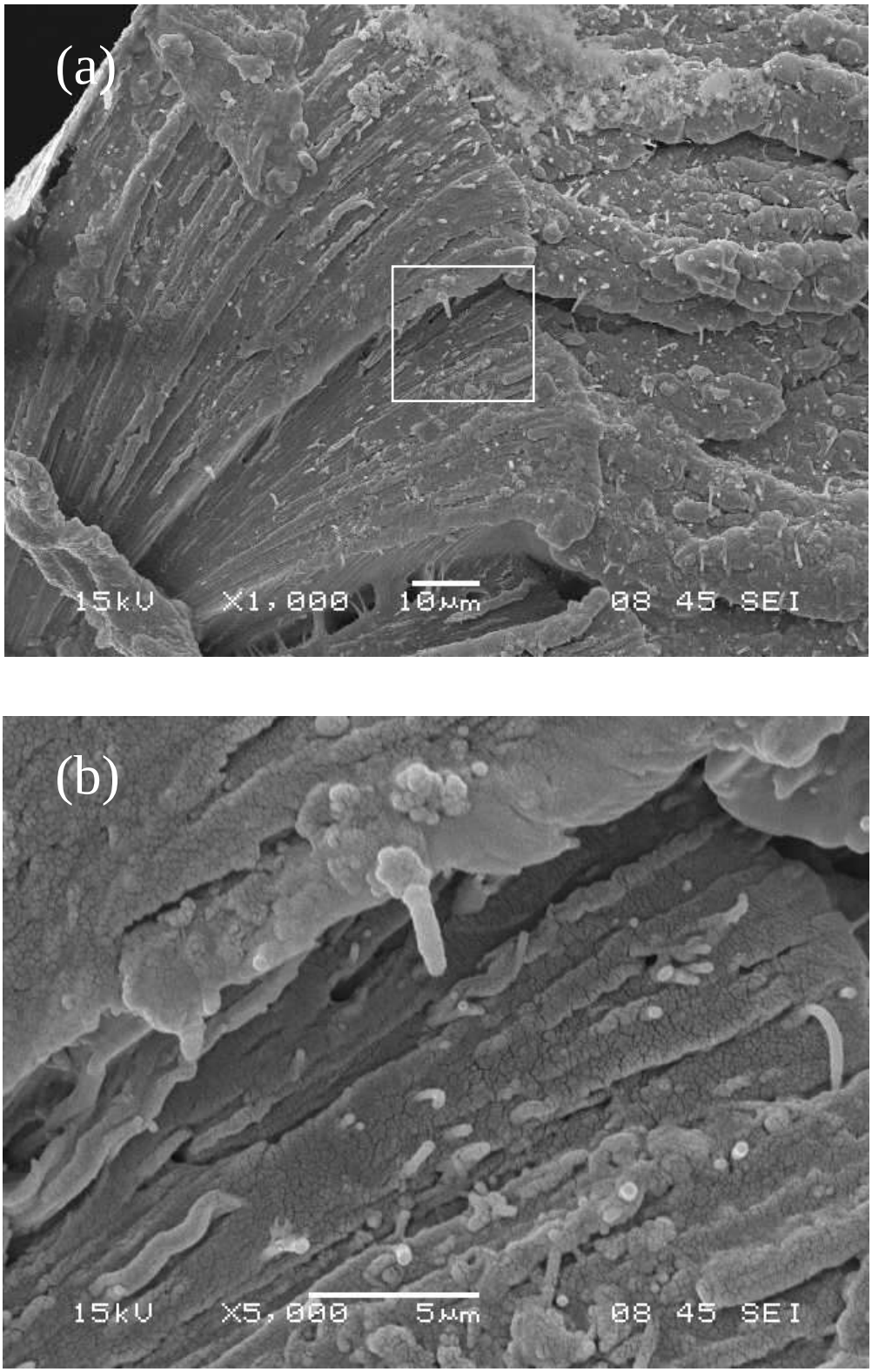

Figure 4.3 Distribution of 1wt% CNT in PETmatrix of PET/CNT nanocomposite fibers at die temperature 290ºC at (a) lower and (b) higher magnifications.

Figure 4.6 shows the yield strength of PET/CNT nanocomposite fibers at different temperatures. It can be observed that the die temperature did not effect the yield strength and all the fibers showed similar average yield strength of 30MPa. Similarly, the die temperature showed no effect on the tensile strength of PET/CNT fibers. Figure 4.7 shows tensile strength of the PET/CNT nanocomposite fibers. An average tensile strength of 78MPa was obtained at all die temperatures. In contrast, the strain at break for as extruded PET/CNT (1wt %) have shown decreasing trend with the increase in die temperature. The strain at break value decreased from 10 mm/mm to 8mm/mm with the increase in die temperature from 265 to 290˚C as shown in Figure 4.8. Similar decreasing trend of the average toughness values was observed with respect to die temperatures as shown in Figure 4.9. Average toughness of 445, 414 and 352 MPa was achieved for extruded nanocomposite fibers at the die temperature of 265, 280 and 290 ˚C, respectively.

Although the die temperature showed little effect on the mechanical properties of as extruded PET/CNT nanocomposite fibers, it showed considerable effect on spinnability of fibers. The spinnability of the fibers can be correlated to the diameter of the spun fibers. Figure 4.10 shows the average diameters of spun fibers at different die temperatures. Smallest diameter fibers with the average diameter of 30 µm were produced at die temperature of 280 °C, whereas, the average fiber diameters of 37 µm and 39 µm were obtained at 265 and 290°C, respectively. It can be concluded that die temperature has an effect on viscosity of PET fiber and a die temperature of 280°C is suitable for melt spinning and melt extrusion process.

Spinning of extruded fibers is known to have impact on alignment of CNT in PET matrix and as a result improves the mechanical properties of PET/CNT nanocomposite fibers [10, 27, 30-32]. Further investigations were carried out on the effect of spinning and CNT concentration on the mechanical properties of PET/CNT nanocomposite fibers while keeping the die temperature fixed at 280 °C.

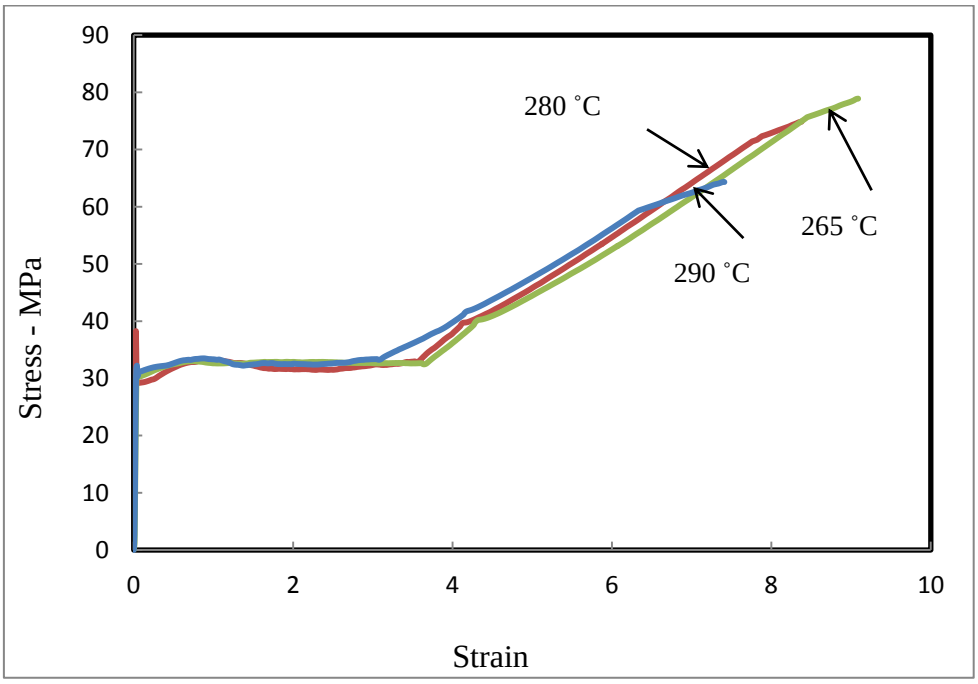

Figure 4.4 Influence of Die temperature on tensile stress strain curve of PET/CNT nanocomposite fibers

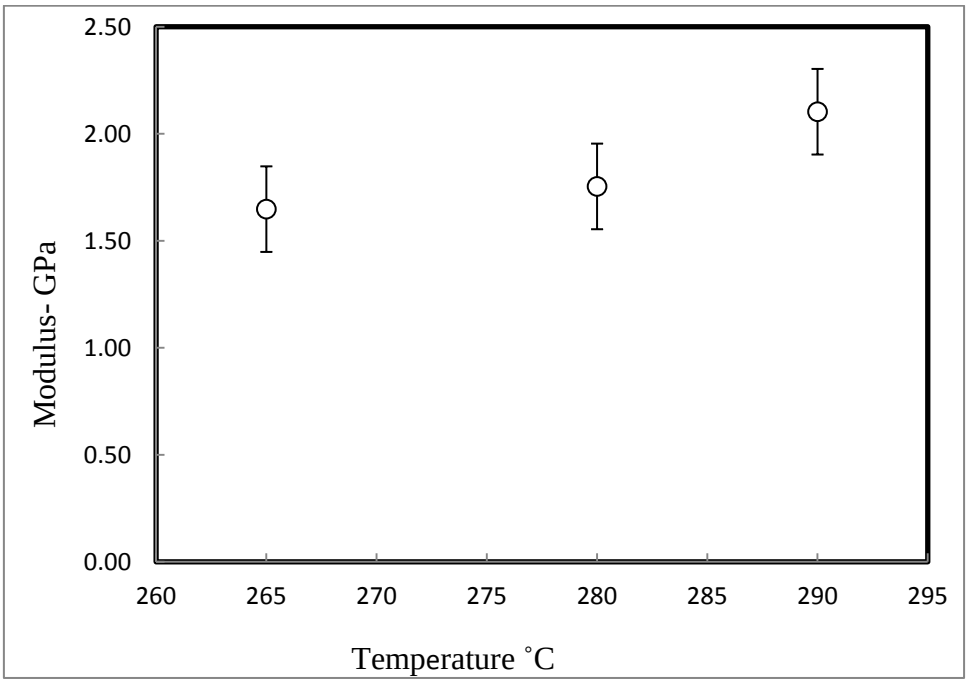

Figure 4.5 Influence of Die temperature on modulus of PET/CNT nanocomposite fibers.

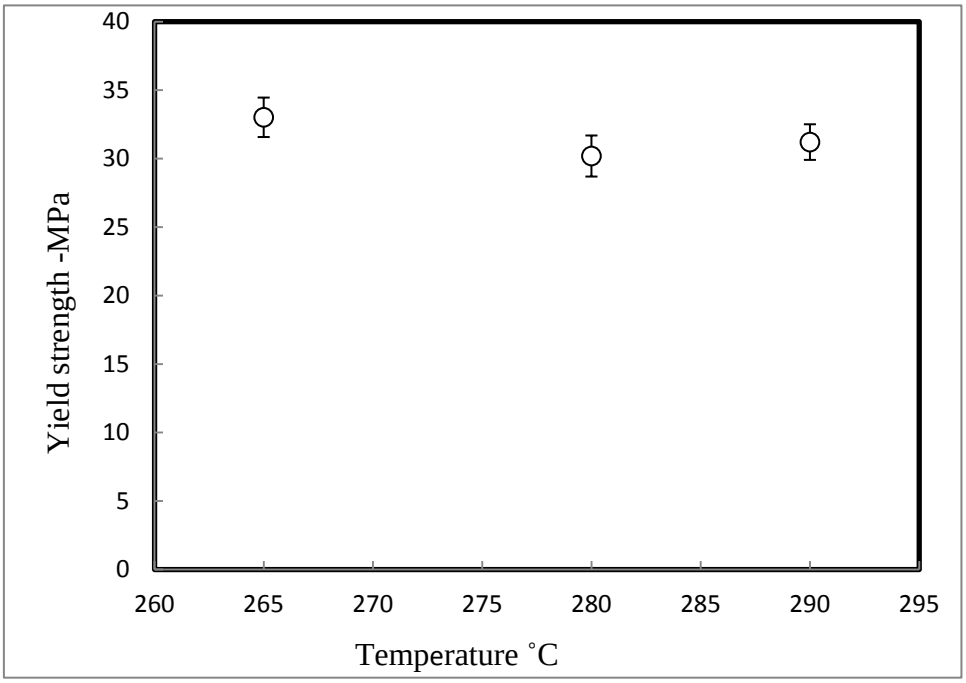

Figure 4.6 Influence of Die temperature on yield strength of PET/CNT nanocomposite fibers.

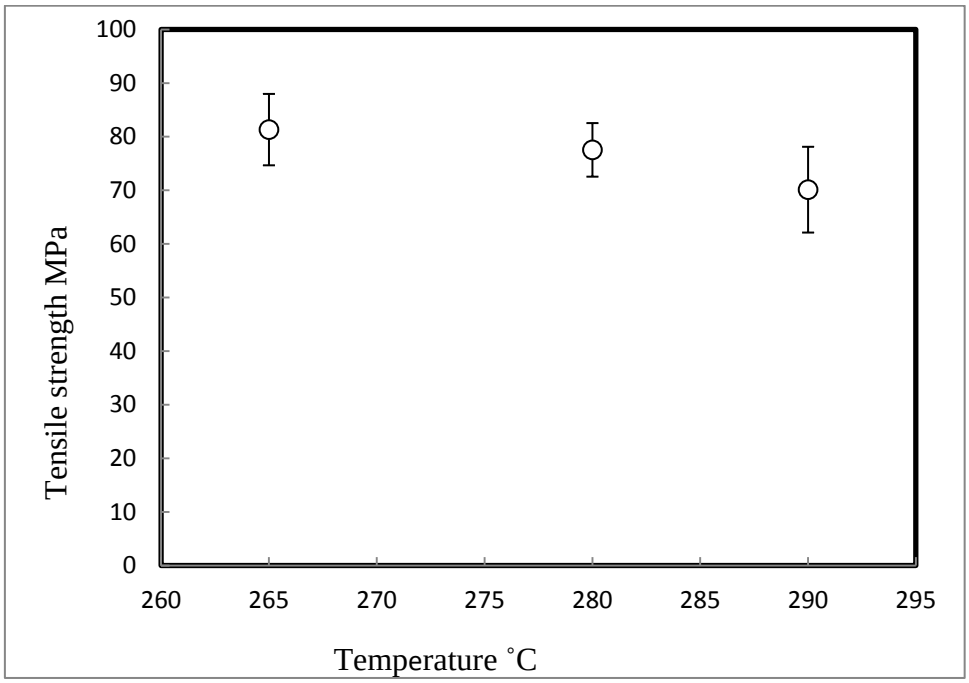

Figure 4.7 Influence of Die temperature on tensile strength of PET/CNT nanocomposite fibers.

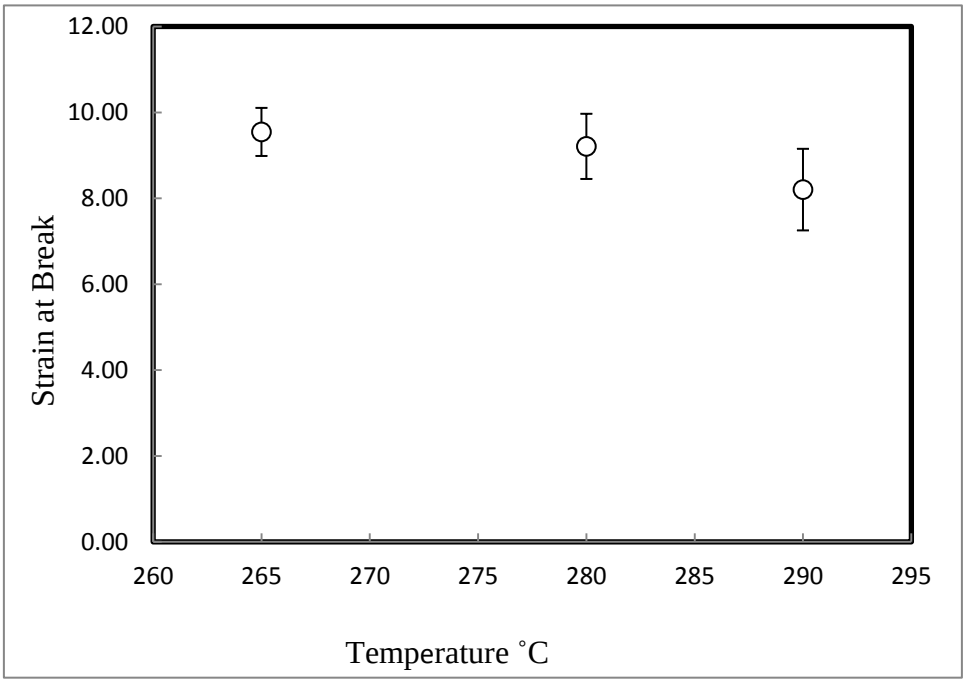

Figure 4.8 Influence of Die temperature on strain at break of PET/CNT nanocomposite fibers.

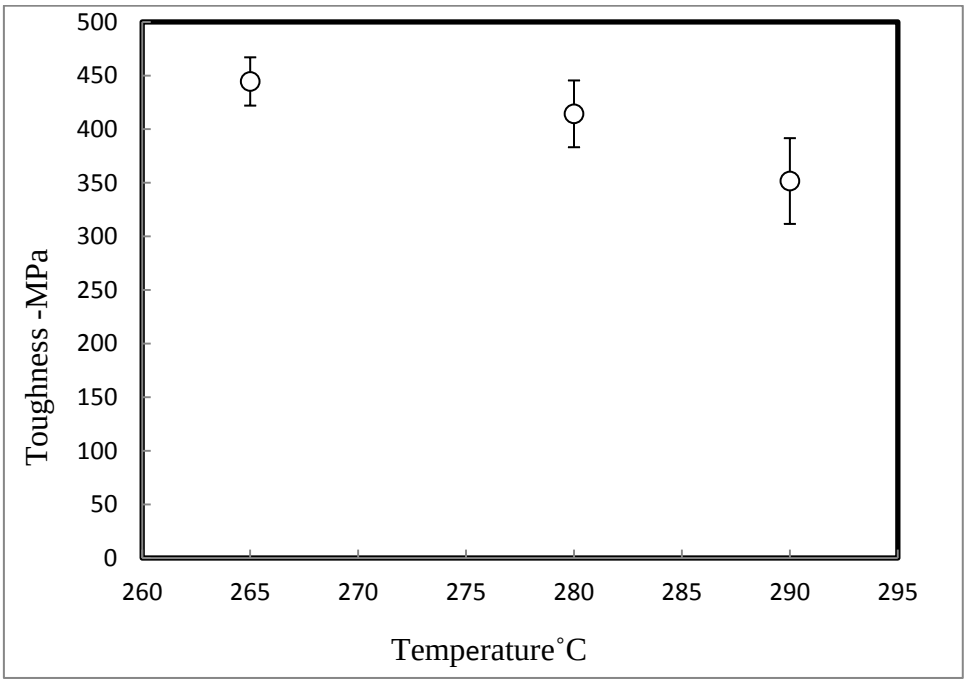

Figure 4.9 Influence of Die temperature on toughness of PET/CNT nanocomposite fibers.

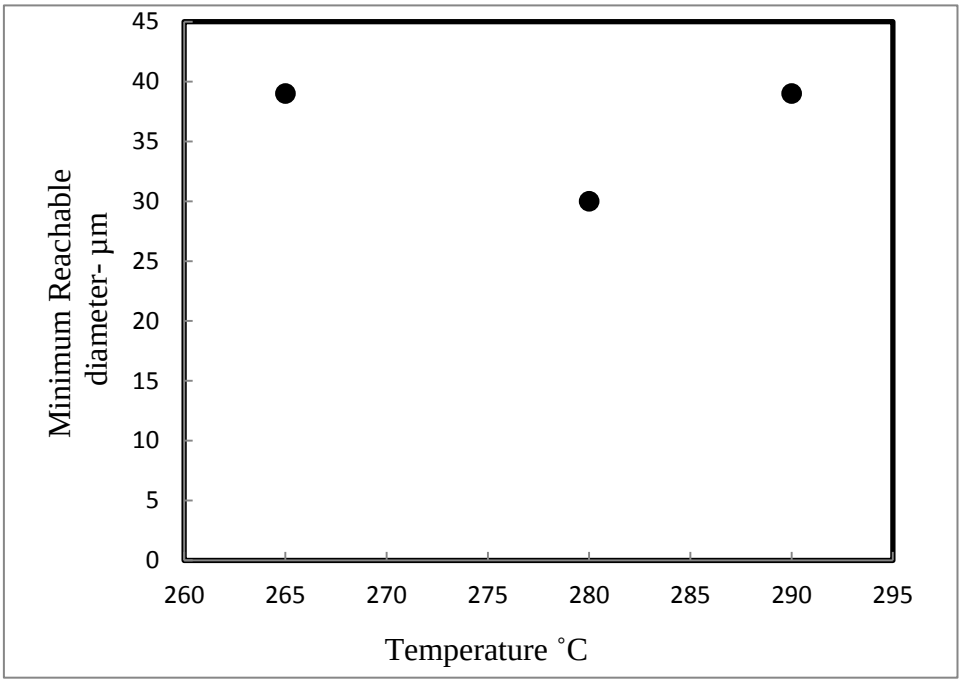

Figure 4.10 Influence of Die temperature on spinnability of PET/CNT nanocomposite fibers.

4.2 Effect of spinning speed on mechanical properties of PET/CNT nanocomposite fibers

4.2.1 Mechanical Properties

PET/CNT nanocomposite fibers were melt spun at different spinning speeds. Extruder temperature profile was fixed at 290 to 275 ˚C and the 1 wt% CNT feeding was fixed at position 1. In previous section, it was observed that melt spinning at die temperature of 280°C produced smallest diameter fiber so the die temperature was fixed to 280°C. Effect of spinning speed on mechanical properties of PET/CNT nanocomposite fibers with 1 wt% CNT was evaluated. Different spinning speeds in the range of 190m/min to 500 m/min were studied. Nanocomposite fibers with average diameter in the range of 32 μm to 51μm were obtained. Figure 4.11 shows the average diameters of fibers obtained at different spinning speeds. Mechanical properties of these nanocomposite fibers are presented in Figure 4.12 to Figure 4.16.

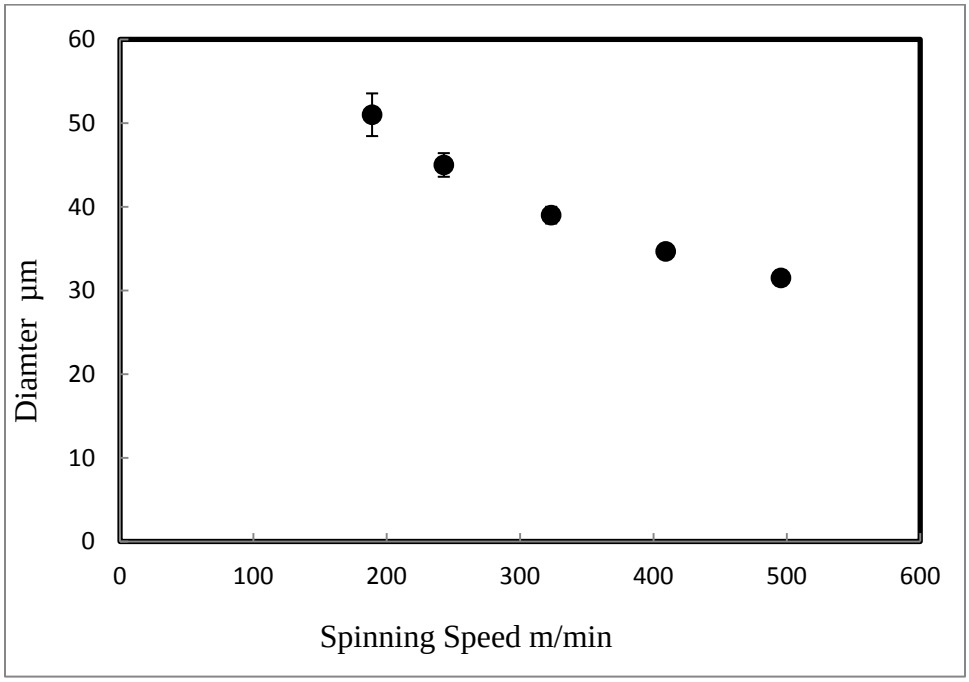

Figure 4.11 Influence of spinning speed on the diameters of PET/CNT nanocomposite fibers.

Figure 4.12 shows the modulus of PET/CNT nanocomposite fibers obtained at different spinning speeds. It can be observed that the fibers spun at highest speed of 500m/min showed better modulus compared to fibers spun at lower speeds. Fibers at this speed have the average modulus value of 2.12 GPa showing 50 % enhancement in modulus value compared to the PET/CNT nanocomposite fibers obtained at the lowest spinning speed 190 m/min. Figure 4.13 shows the yield strength of the PET/CNT nanocomposite fibers spun at different speeds. Average yield strength of 31MPa was obtained at spinning speed of 500 m/min. This value is 24% better than the yield strength of fibers obtained at 190m/min. Tensile strength of PET/CNT nanocomposite fibers with respect to spinning speeds is shown in Figure 4.14. It was observed that tensile strength increases with the

spinning speeds. Tensile strengths of the nanocomposite fibers spun at spinning sppeds of 500, 410, 320, 240 and 190 m/min are 61, 54, 50, 49 and 47 MPa, respectively. An improvement of 30% in tensile strength of nanocomposite fibers was observed at highest speed of 500m/min compared to lowest speed of 190m/min.

The improvement in modulus, yield strength and tensile strength values with the increase in spinning speed is attributed to the improvement of both PET molecular chain alignment and CNT alignment along the length of PET/CNT nanocomposite fibers. Spinning of PET/CNT fibers also improves the dispersion of CNT in PET matrix. Similar conclusions on the improvement of mechanical properties of polymer/CNT fibers due to good dispersion and alignment of CNT in spun fibers were drawn in recent works [10, 18, 29]. Mun et al. [18] reported that initial modulus of PET/modified Ph3P-MWCNT hybrid fibers containing 1wt% modified CNT found to increase linearly with increasing draw ratio (spinning speed). The modulus value at higher spinning speed was 4.75GPa and 2.89GPa at lower spinning speed. However, they have documented that the tensile strength of these nanocomposite fibers decreased from 60MPa at low spinning speed to 26MPa at high spinning speed (spinning speed). Likewise elongation at break was reduced from 3 to 1 %. Mazinani et al. [10] reported that modulus of PET/CNT containing 1wt% commercialized CNT improved from 1.4 GPa to 2GPa owing to draw ratio. Tensile strength increased from 60 to 120 MPa due to spinning speed. Perrot et al. [30] produced the polyamide 12 /CNT spun nanocomposite fiber containing 7 wt% CNT. They reported that for these nanocomposite fibers the modulus improved from 1.7GPa to

5.1GPa but in this case the fibers were hot drawn after spinning. Tensile strength improved from 117 to 389MPa due to spinning and hot drawing of these nanocomposite fibers.

Figure 4.15 and Figure 4.16 represents the variation of strain at break and toughness with the spinning speed. Strain at break showed decreasing trend with the increase of spinning speeds up to speed of 320 m/min. The strain at break values decreased from 3.9 mm/mm to 2.9mm/mm when the spinning speed increased from 190 to 320 m/min. The strain at break remained constant with further increase in spinning speed from 320 to 500m/min. Similarly, toughness values showed moderate decrease with the increase of spinning speed from 189 to 320 m/min, however an increase in the toughness values were obtained when the spinning speed increased further from 320 to 500m/min as shown in Figure 4.16. Maximum toughness of 129 MPa and 132MPa was achieved for the fibers having diameter 32 μm and 51μm, respectively. The decrease in the strain at break and toughness is attributed to the increase in the stiffness of PET/CNT nanocomposite fibers with the increase in spinning speeds. Similar effect has been observed elsewhere [18, 30].

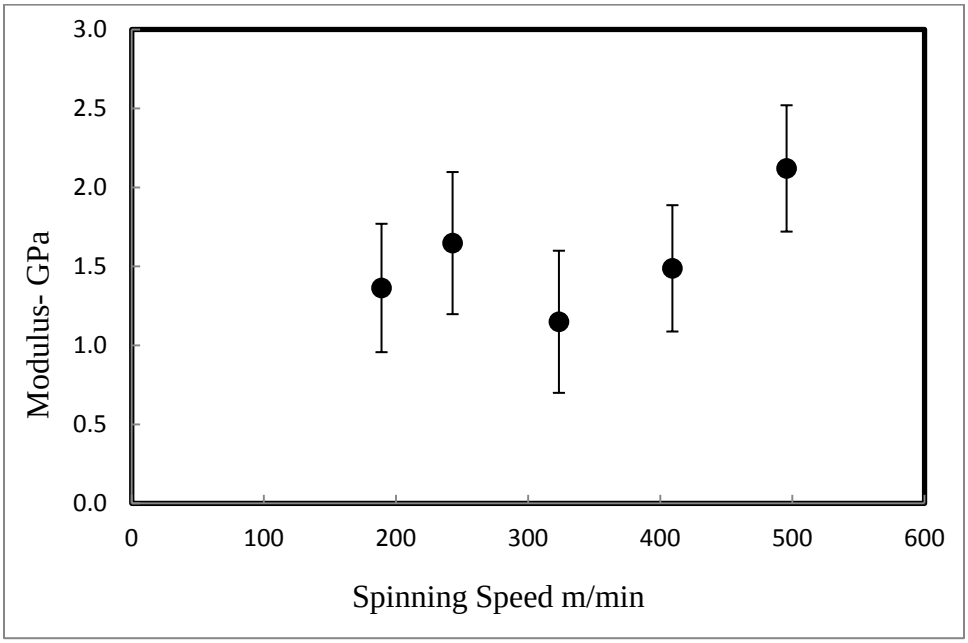

Figure 4.12 Influence of spinning speed on the modulus of PET/CNT nanocomposite fibers.

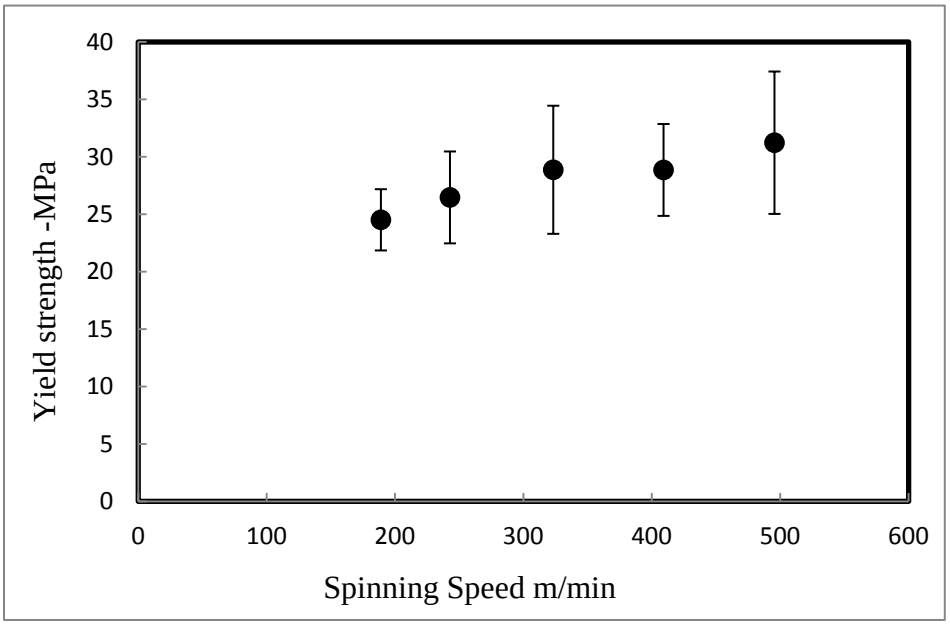

Figure 4.13 Influence of spinning speed on the yield strength of PET/CNT nanocomposite fibers.

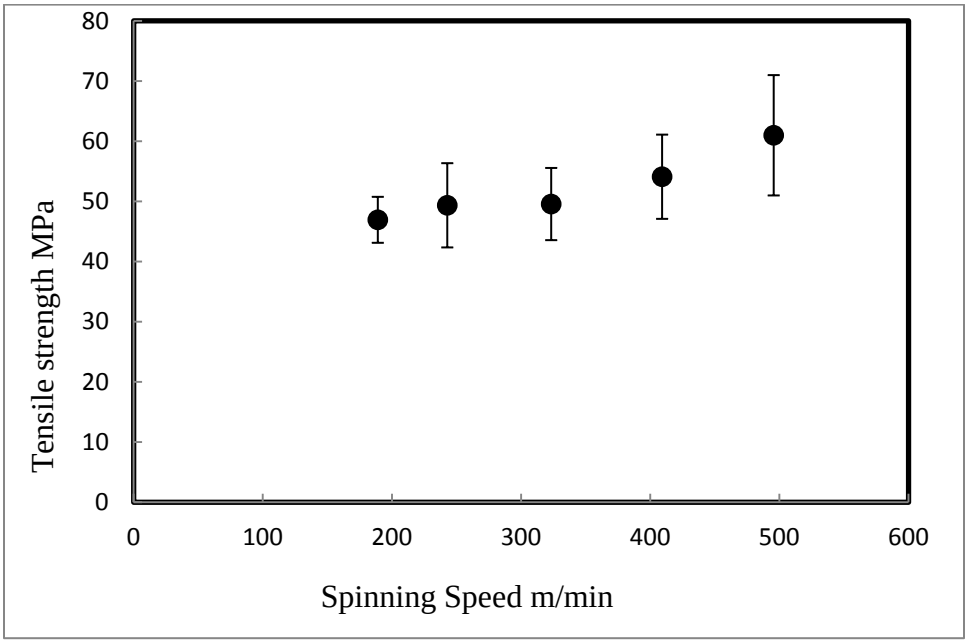

Figure 4.14 Influence of spinning speed on the tensile strength of PET/CNT nanocomposite fibers.

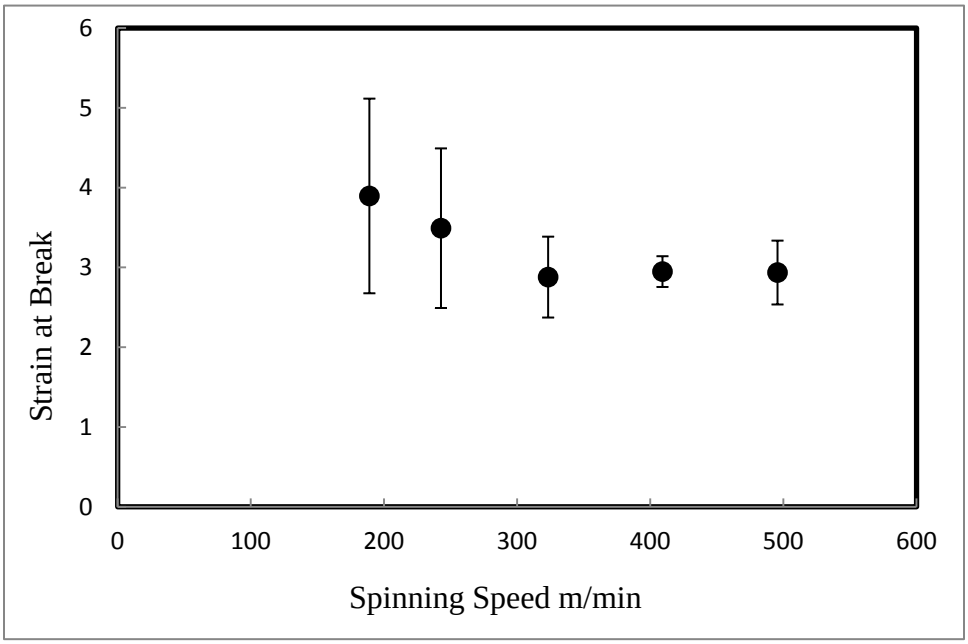

Figure 4.15 Influence of spinning speed on the strain at break of PET/CNT nanocomposite fibers.

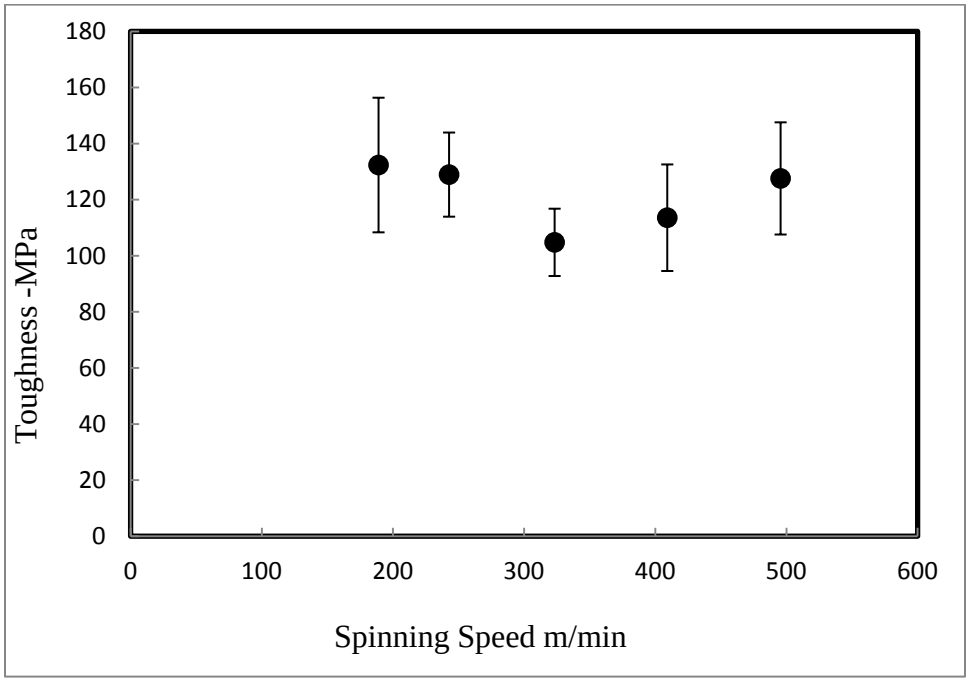

Figure 4.16 Influence of spinning speed on the toughness of PET/CNT nanocomposite fibers.

4.3 Influence of CNT concentration on the Mechanical properties of extruded PET/CNT nanocomposite fibers

4.3.1 TG-DSC Analysis

The aligned and high aspect ratio MWCNT (Figure 3.1) of 20 to 50 nm diameter and length of 200 to 500nm was used to reinforce the PET. The CNT and the PET materials were fed into the extruder through the separately controlled feeders. The feeder speed was calibrated to obtain appropriate proportion of CNT and PET materials. The PET material was melt and mixed with CNT in the extruder and the PET/CNT nanocomposite fibers were produced. The weight percent of CNT was confirmed by TG-DSC test. Figure 4.17 shows the TG-DSC curves obtained from the analysis of pure PET fiber, pure CNT and PET/CNT nanocomposite fiber. The results show negligible weight loss between ambient and 300 °C. Above 300 °C the pure PET fiber decomposes in a single step at around 425 °C. This weight change corresponds to the decomposition of the base polymer to leave residual carbon char from the polymer backbone. This carbon char is quantified at 750 °C where the weight profile is a plateau and does not change under inert nitrogen atmosphere. The CNT is stable until 900 °C and then starts to gradually decompose. Thus, for a composite fiber at 750 °C, the weight percent of residue corresponds to the weight of polymer char and the CNT. The CNT concentration of 0.1, 0.5, 1, 2.7, 3 and 7.5 wt% has been analyzed. In order to accurately quantify the CNT concentrations in PET/CNT nanocomposite fibers, new TG samples were prepared using measured amount of PET and CNT. The results of weight percentage obtained for the

fibers were compared with well prepared samples of known concentration of CNT and PET fiber. The results were in good correlation with the percentages set for the CNT feeder as shown in Figure 4.18. Therefore, the experimental set up (twin screw extruder) is in good agreement to obtain required amount of CNT in PET/ CNT nanocomposite fibers.

4.3.2 SEM Analysis

The twin screw extruder has three consecutive stage of mixing elements that helped in obtaining homogenous mixture of PET/CNT nanocomposite. The fractured surface of pure PET fibers is shown in SEM micrograph Figure 4.19. The distribution of CNT in PET/CNT nanocomposite fibers was confirmed by SEM micrographs shown in Figure 4.20 to Figure 4.24. It can be observed that samples with 0.5% (Figure 4.20) and 1% CNTs (Figure 4.21) have uniform distribution and alignment of CNTs. The samples with higher CNT percentages showed agglomeration of CNTs, in which, sample with 2.7wt% CNTs (Figure 4.23) showed better distribution compared to 3% (Figure 4.22) and 7.5% CNTs (Figure 4.24). It is also observed that high CNT concentrated fibers (2.7 and above) shows many small voids. The number of these voids increased with CNT concentration. The distribution of CNT has impact on mechanical properties.

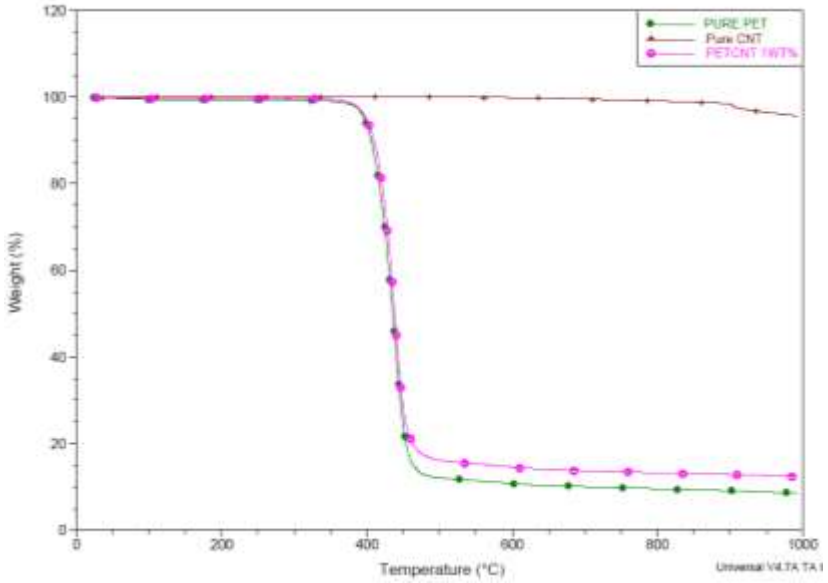

Figure 4.17 TGA- Thermograms showing the weight change of pure PET, pure CNT and PETCNT 1wt%.

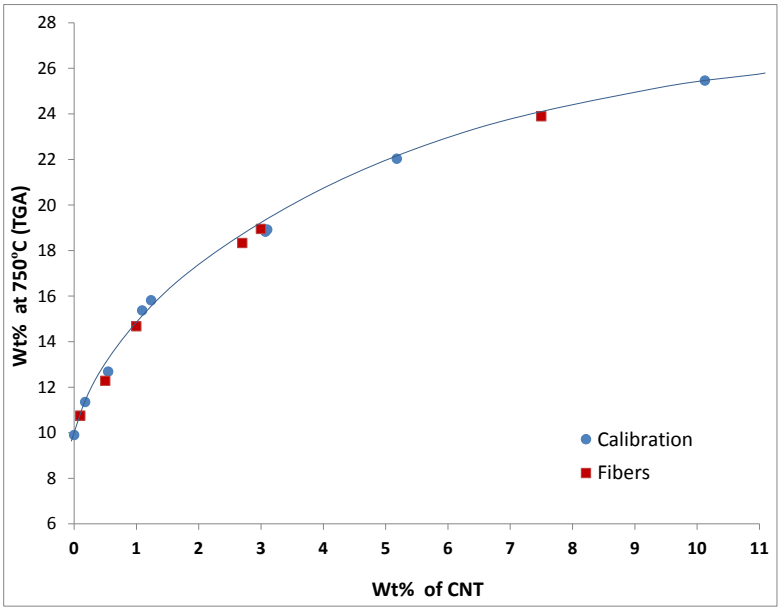

Figure 4.18 TGA calibration and the CNT concentrations of the produced nanocomposite fibers.

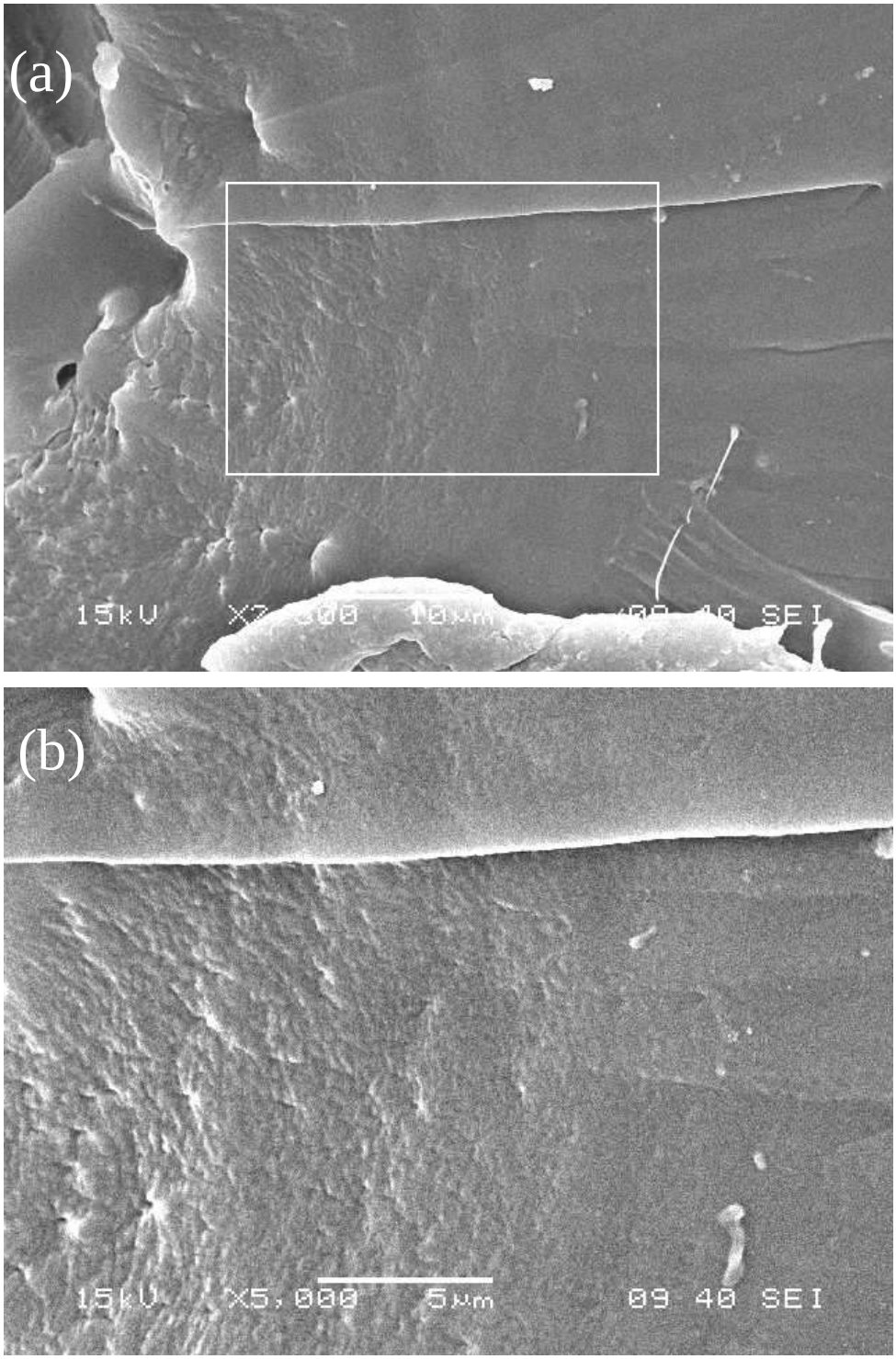

Figure 4.19 Fracture surface of Pure PET fibers at (a) lower and (b) higher magnifications.

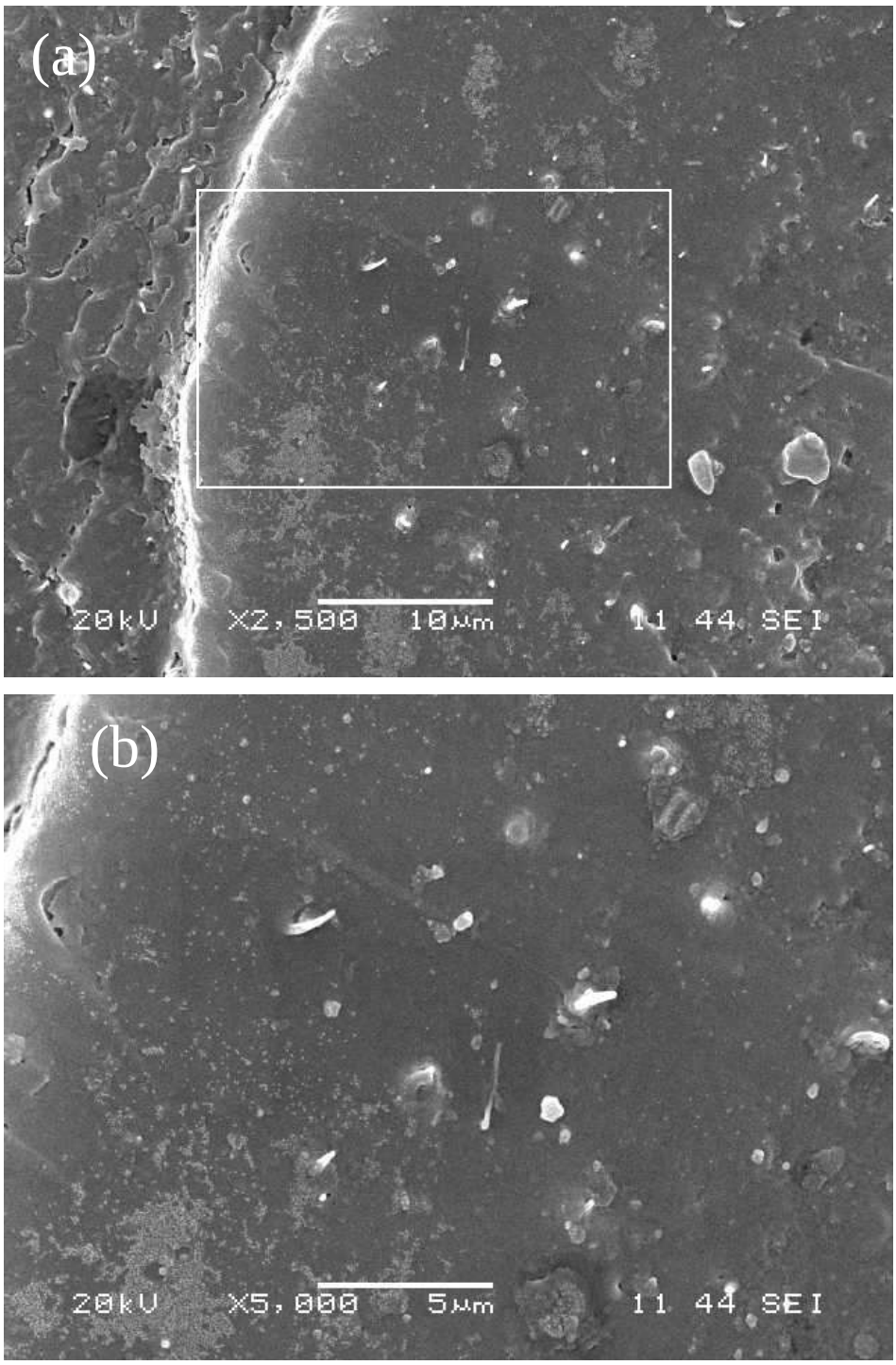

Figure 4.20 Distribution and alignment of 0.5wt% CNT in PET/CNT nanocomposite fibers at (a) lower and (b) higher magnifications.

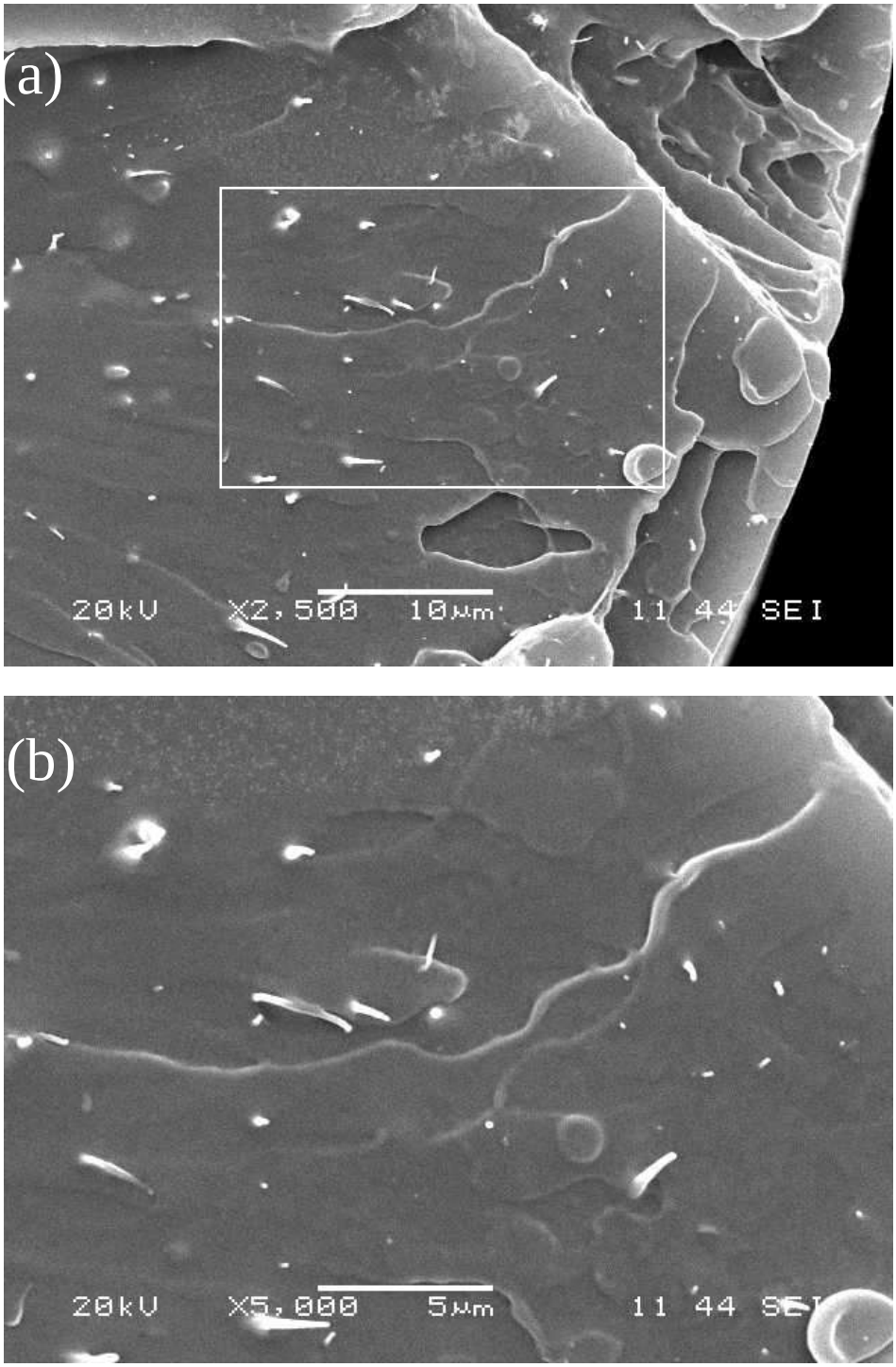

Figure 4.21 Distribution and alignment of 1wt% CNT in PET/CNT nanocomposite fibers at (a) lower and (b) higher magnifications.

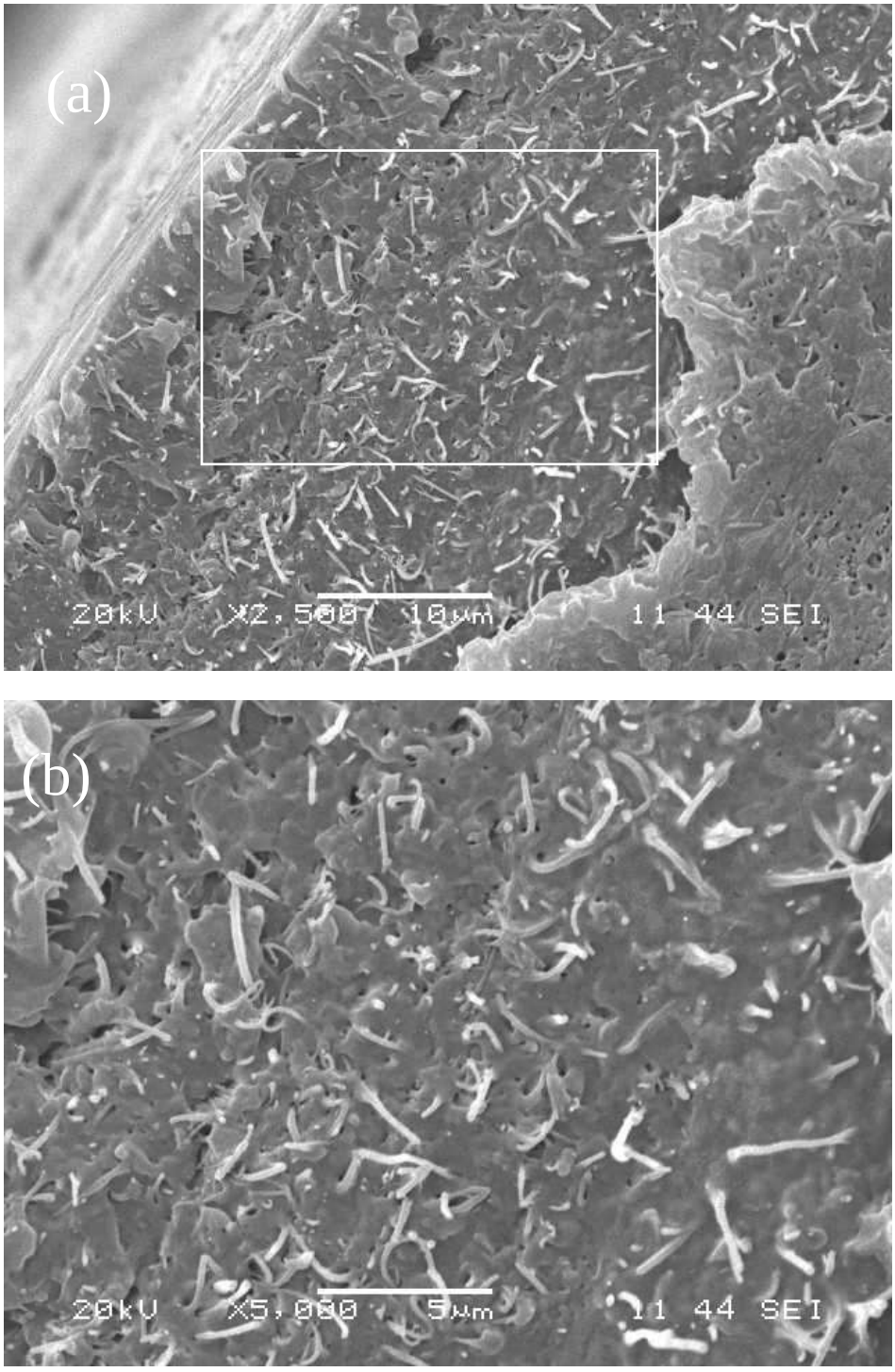

Figure 4.22 Distribution and alignment of 2.7wt% CNT in PET/CNT nanocomposite fibers at (a) lower and (b) higher magnifications.

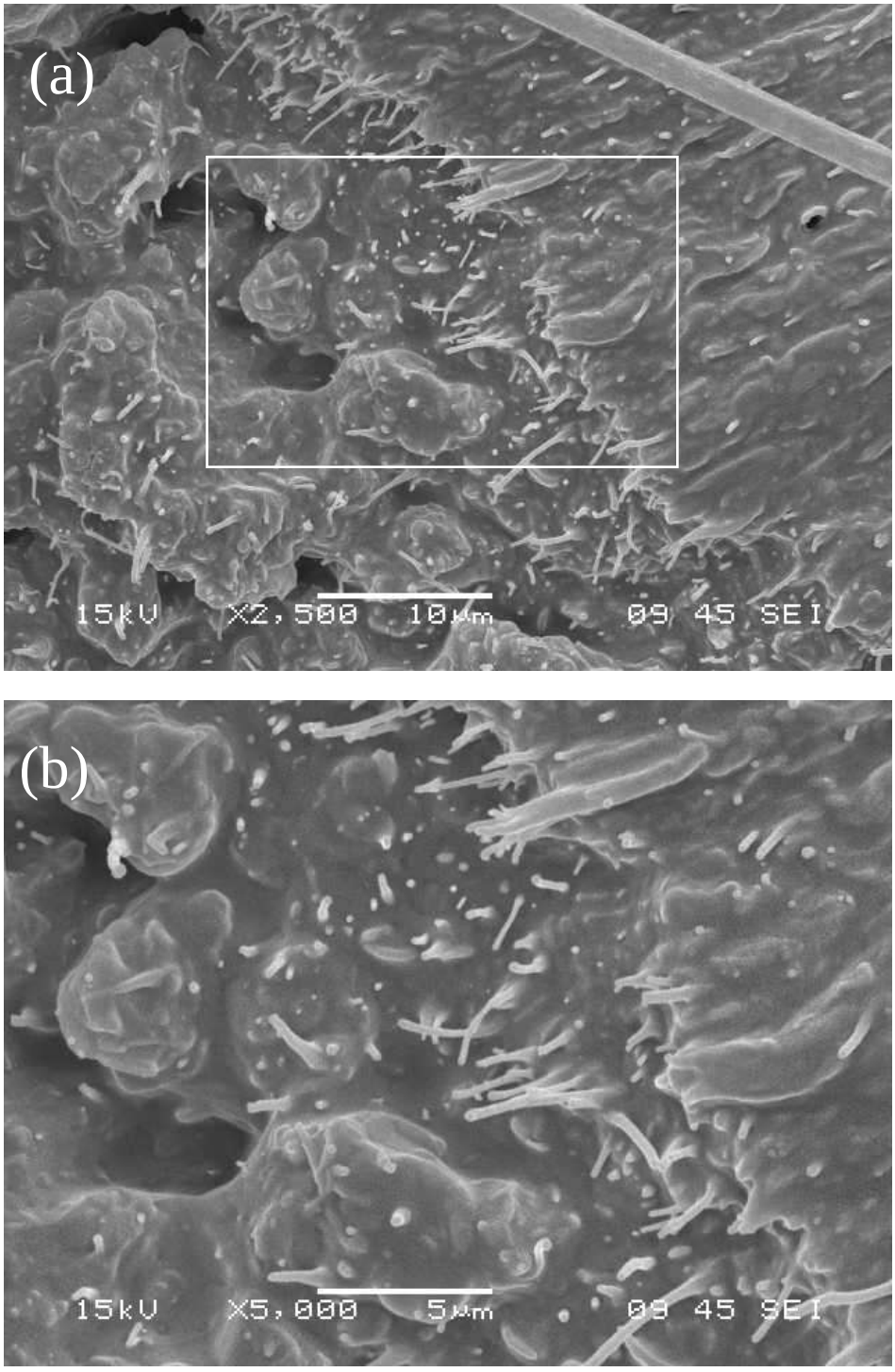

Figure 4.23 Distribution and alignment of 3.0wt% CNT in PET/CNT nanocomposite fibers at (a) lower and (b) higher magnifications.

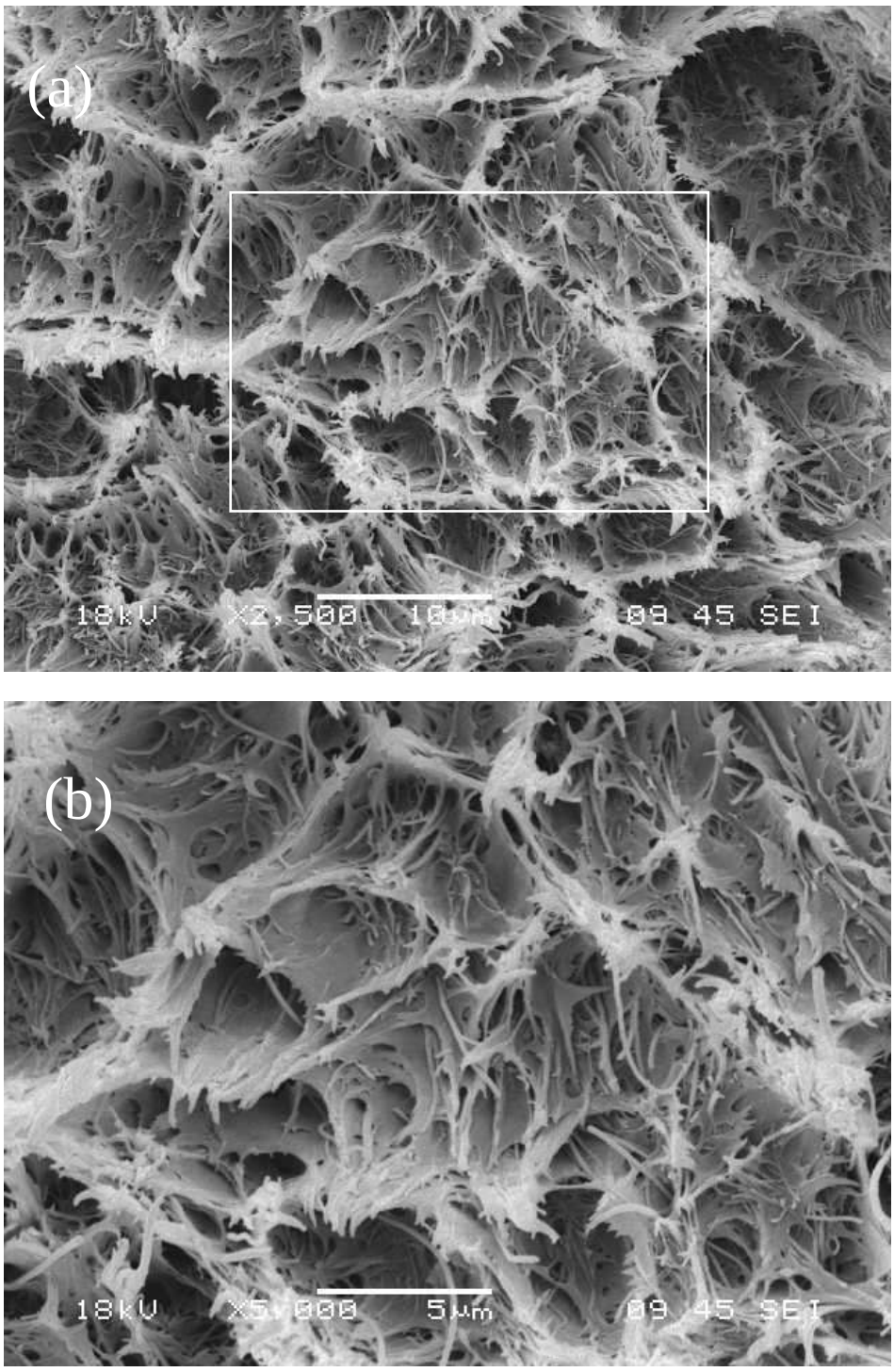

Figure 4.24 Distribution and alignment of 7.5wt% CNT in PET/CNT nanocomposite fibers at (a) lower and (b) higher magnifications.

4.3.3 Mechanical Properties

The tensile stress strain curve for extruded PET/CNT nanocomposite fibers with different CNT concentrations is shown in Figure 4.25. Figure 4.26 shows the effect of CNT contents on the modulus of the extruded PET/CNT nanocomposite fibers. It can be seen that the average modulus of PET/CNT nanocomposite fibers is increasing with the CNT loading in PET matrix. This increase varies from 2% at 0.1 wt% CNT to 170% at 7.5 wt% CNT. The improvement is attributed to the high stiffness and aspect ratio of CNT in PET matrix the same was evident from Mun et al. [18] and Jun et al. [33] work for extruded fiber. Mun et al. documented that the modulus of pure PET increased from 2.21 to 3.14GPa due to addition of 1.5 wt% modified Ph3P-MWNT in PET matrix i.e. increment of about 42%. Likewise Jun et al. reported that 12.3 and 17.4 % increment in the modulus of pure PET of 1.55GPa due to adding of 1.0wt% pristine CNT and modified c-CNT into PET matrix, respectively.

The yield strength of pure PET fibers (35MPa) was enhanced by the addition of more than 1wt% CNT concentration into PET matrix as shown in Figure 4.27. A 30 % improvement was observed with addition of 2.7 and 3.0 wt% CNT. A 54% enhancement in average yield strength was observed in samples of 7.5 wt% CNT fibers. However, for concentrations up to 1.0 wt% the average yield strength did not improve (Figure 4.27).

Figure 4.28 shows the influence of CNT loading on tensile strength of extruded PET/CNT nanocomposite fibers. Loading of 0.1 wt% CNT significantly improved the

tensile strength of pure PET fibers by 90%. Similarly, other CNT concentrations such as 0.5, 1, 2.7, 3, and 7.5 wt% increased the tensile strength by about 53, 53, 27, 16 and 31%, respectively. Good distribution and interfacial bond of CNT in the PET matrix can be observed in SEM micrographs of Figure 4.20 to Figure 4.23 which improved the strengths of these nanocomposite fibers. The white colour in the SEM micrographs represents the CNT. The pulled out CNT indicates a good adhesion between the CNT and PET matrix. Therefore PET/CNT has good interfacial bonding, which increases the strength of the nanocomposite fiber. This effect is more significant for low content of CNT but reduces as CNT concentration increases because of due to increase in the agglomeration of CNT in the polymer matrix. Similar effect of the present study has been documented in the Jun et al. [33] investigation. They reported that the improvement in the tensile strength of pure PET of 60.4 MPa was about10% and 29%. Further, they reported that these improvements in the tensile strength owed to presence of uniformly distributed 1wt% pristine CNT and modified c-CNT in PET matrix, respectively. In addition, in our recent study[29] it was observed that the good distribution and adhesion of CNT in LLDPE matrix obtained the improvement of about 38% (350MPa) in the tensile strength of LLDPE/CNT nanocomposite fibers, compared to pure LLDPE fiber, but these fiber were drawn at room temperature. In other Studies, quite similar work being done by Mazinani et al. [10] but have shown adverse effect in the tensile strength of PET/CNT nanocomposite extruded fibers, compared to pure PET fiber due to presence of agglomerated CNT in the PET matrix.

An improvement in the strain at break was also observed with the addition of different CNT concentration except for the 7.5wt% as shown in Figure 4.29. The addition of 0.1, 0.5, 1, 2.7 and 3wt% CNT in PET matrix, increased the average strain at break by 173, 175, 132, 73 and 50 %, respectively, compared to pure extruded PET fibers (4mm/mm). Likewise, the effect of CNT concentration on the toughness of nanocomposite fibers is shown in Figure 4.30. Toughness of as extruded pure PET fibers (157MPa) was enormously improved to 604 MPa (285%), 556 MPa (254%), 414 MPa (164%), 314 MPa (100%) and 261MPa (66%), with the addition of 0.1, 0.5, 1, 2.7 and 3wt% CNT, respectively. Compared to pure PET fibers, the improvement in the strain at break and toughness of extruded nanocomposite fibers were due to presence of randomly oriented CNT. During tensile testing of these fibers, initially the CNTs pulled and partially oriented with molecular chains towards the tensile direction. Further elongation of PET/CNT nanocomposite fibers aligned the CNT in the PET matrix, as a result CNT held the PET matrix together for improving strain at break and toughness. However, the strain at break and toughness values of PET/CNT nanocomposite decreased with increased content of CNT in PET matrix due to agglomeration of CNT and formation of voids. More number of voids observed for 7.5wt% CNT in PET/CNT nanocomposite fibers compared to any other CNT contents. Therefore, drastic decrement in strain at break and toughness with a loading of 7.5 wt% CNT was observed due to presence of large amount of voids in the PET/CNT nanocomposite fibers (Figure 4.24). In addition, some studies [10, 34] indicate that increasing CNT content in polymer matrix increases the

agglomeration of CNT in the matrix. This results in voids formation around the nanotubes during tensile test which makes the fibers weaker and thereby decreases the strain at break and toughness of PET/CNT nanocomposite fibers.

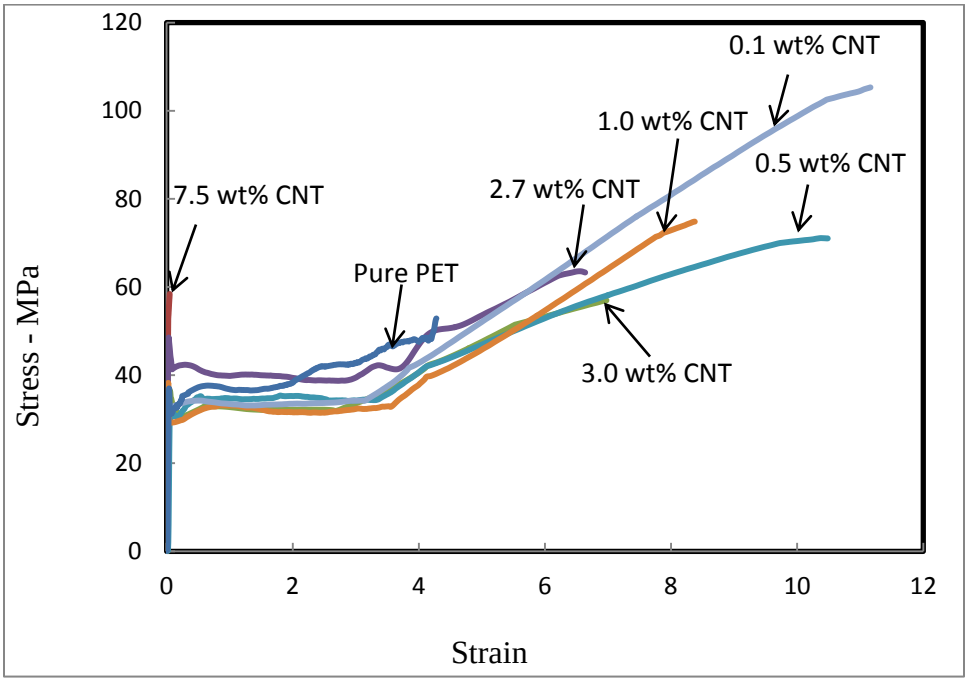

Figure 4.25 Influence of CNT concentration on the Mechanical properties of extruded PET/CNT nanocomposite fibers

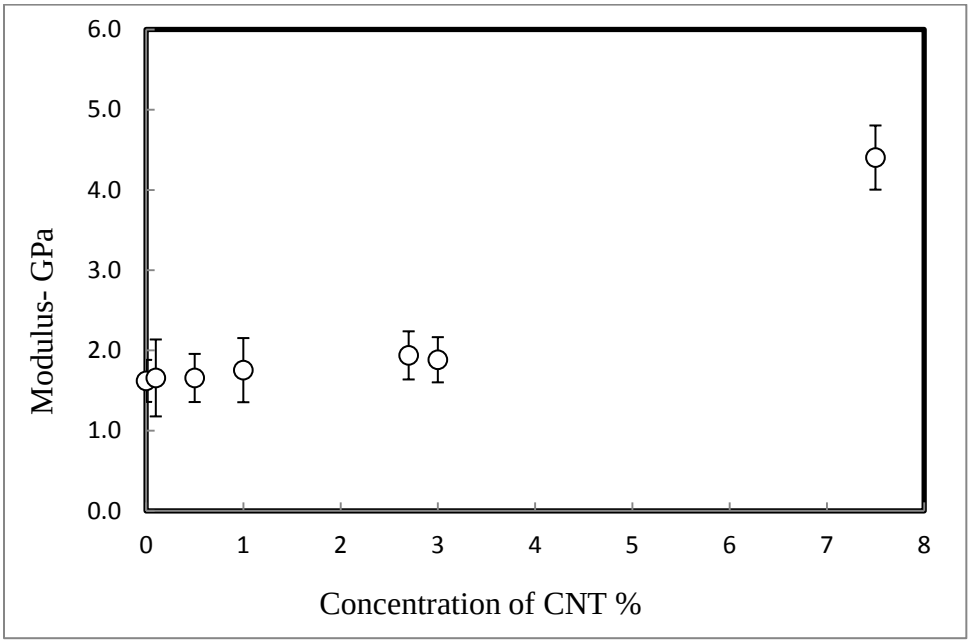

Figure 4.26 Influence of CNT concentration on the modulus of extruded PET/CNT nanocomposite fibers.

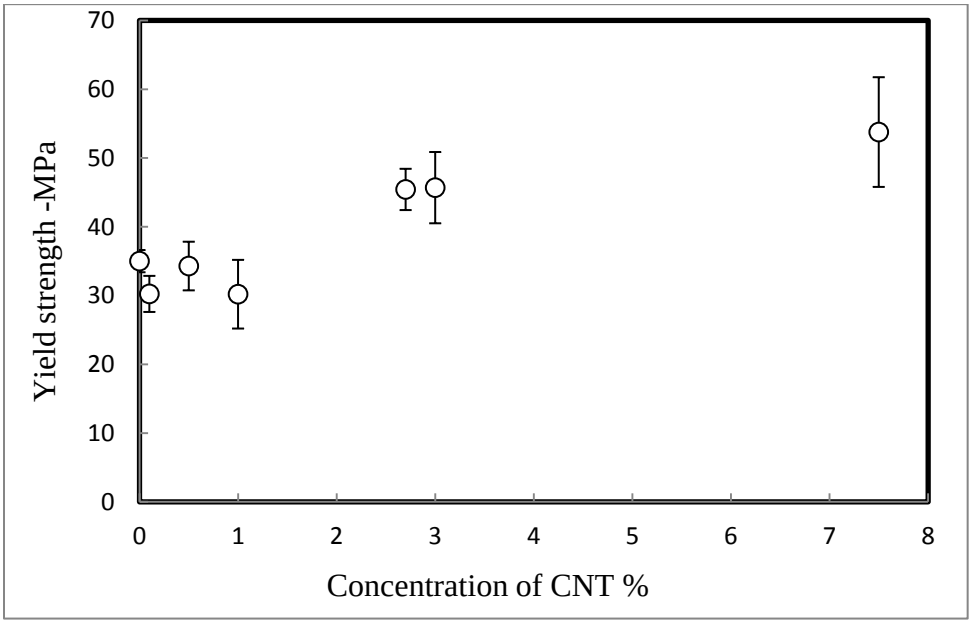

Figure 4.27 Influence of CNT concentration on the yield strength of extruded PET/CNT nanocomposite fibers.

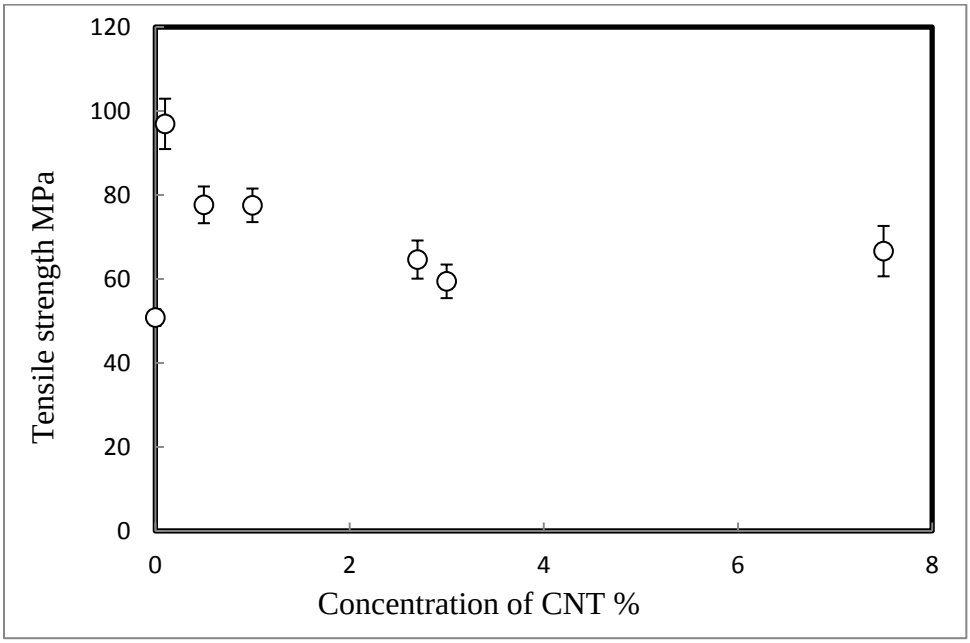

Figure 4.28 Influence of CNT concentration on the tensile strength of extruded PET/CNT nanocomposite fibers.

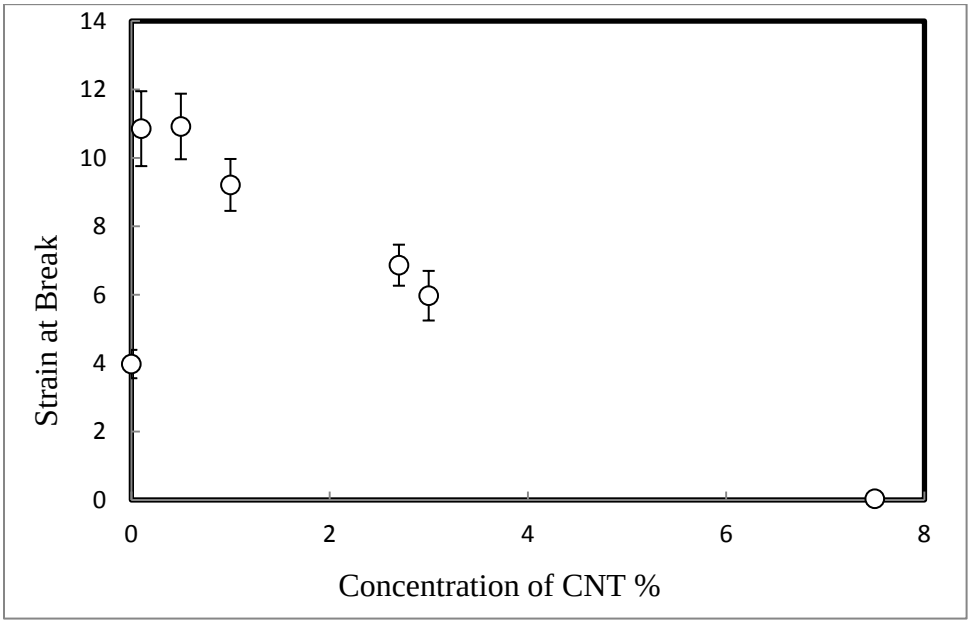

Figure 4.29 Influence of CNT concentration on the strain at break of extruded PET/CNT nanocomposite fibers.

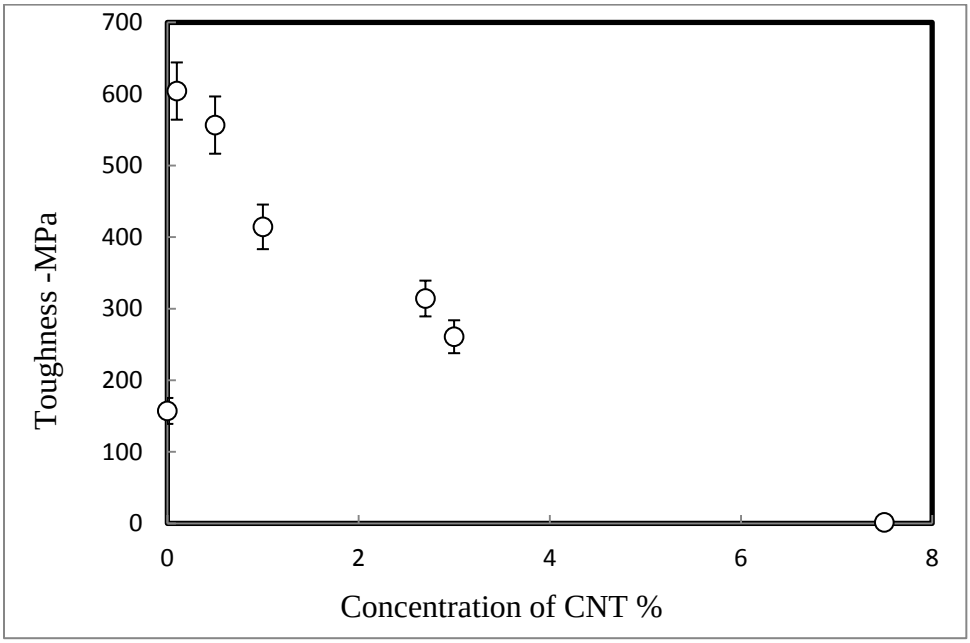

Figure 4.30 Influence of CNT concentration on the toughness of extruded PET/CNT nanocomposite fibers.

4.4 Effect of CNT concentration on the mechanical properties of spun PET/CNT nanocomposite fibers.

The PET/CNT nanocomposite fibers with different CNT concentration have been melt spun and the mechanical properties of the spun PET/CNT nanocomposite fibers were studied. To draw a comparison the pure PET fibers was also produced by melt spinning process. The pure PET and PET/CNT nanocomposite fibers were spun at different spinning speed to achieve the minimum possible diameter without any fiber fracture. The minimum diameter is expected to have well aligned CNT in the PET/CNT nanocomposite fibers. The pure PET and PET/CNT nanocomposite fibers containing 0.1 and 0.5wt% of CNT reached the minimum diameters of 20 μm at spinning speed of 2200m/min. Nanocomposite fibers containing 1 and 2.7 wt% CNT reached minimum diameter of about 30 and 50 μm, respectively. However, it was observed that the PET/CNT nanocomposite fibers with higher concentration such as 3 and 7.5 wt% CNT had poor spinnability due to more frequent fracture of these fibers. The mechanical properties of the spun fibers were determined from the tensile test results. It was observed that low concentration CNT (up to 0.5 wt% CNT) have shown significant improvement in the tensile properties as presented in Figure 4.31 to Figure 4.35. On the other hand, higher concentration of CNT showed an adverse effect on the mechanical properties.

The influence of CNT concentration on the mechanical properties of spun pure PET and spun PET/CNT nanocomposite fibers is shown in Figure 4.31 to Figure 4.35. The fibers of 20 μm diameter with low CNT content of 0.1 and 0.5 wt% CNT have shown

remarkable increment of about 16 and 56% in the modulus, compared to pure PET spun fibers with a modulus of 8.6 GPa. The fibers of 20 μm diameter have the highest value compared to other fibers. Further, yield strength increases with an addition of 0.1 wt% CNT and later decreases for 0.5wt % CNT. About 15% improvement in the yield strength is observed for PET/CNT nanocomposite spun fibers with 0.1wt% CNT addition. A very low content of 0.1wt% CNT has significant influence on the tensile strength of the PET/CNT nanocomposite spun fibers (obtained at 2200m/min spinning speed). An improvement of 40% (532MPa) in tensile strength of PET/CNT nanocomposite spun fibers is achieved with the addition of 0.1wt% CNT in PET matrix, compared to pure PET fibers of 380MPa. The improvement in the modulus for nanocomposite fibers with smaller diameter is attributed to the good distribution, and high aspect ratio and alignment of CNT in the PET matrix [18, 27, 29]. Moreover, the obtained modulus value for 0.1 and 0.5 wt% CNT is close to the average theoretical modulus obtained by the rule of mixtures to have a value of 10 and 15 GPa, respectively. Furthermore, theoretical value is obtained by presuming the CNT are well aligned and continuous. Therefore, CNT in these fibers are well aligned in the PET/CNT nanocomposite fibers, due to melt spinning at high speed. The increment in the tensile properties is due to good adhesion between the CNT and PET interface. It was observed in low content of 0.1wt% CNT and later it is decreased with increasing CNT content. This decrement is due to formation of voids during melt spinning. The Higher the CNT contents the more void formation in PET/CNT nanocomposite fibers is observed. Similar effect has been shown by Mun et al.

[18] that adding low content of 0.5wt% Ph3P-MWNT has the highest tensile strength of 64 MPa, which is about 40% higher than that of pure PET (46 MPa). Later, after critical loading, the addition of 1.5wt% Ph3P-MWNT has reduced the strength to 57MPa due to agglomeration of CNT. However, PET/CNT nanocomposite fibers of 20μm diameter have a lower strain at break due to the addition of 0.1 and 0.5 wt% CNT in the PET matrix. The PET/CNT nanocomposite spun fibers with 0.1 and 0.5 wt% CNT have a strain at break of 0.8 and 1.3 mm/mm, respectively. The pure PET fibers have strain at break of 1.4mm/mm and the average toughness is 310MPa. The addition of 0.1 and 0.5 wt% CNT decreased toughness to 260 and 152MPa, respectively. This decrement is due to decrease in the strain at break of PET/CNT nanocomposite fibers.

The spun nanocomposite fibers with 30 μm diameters for 0.1 and 0.5 wt% CNT content have shown an improvement in the modulus by 10% (3.05GPa) and 54% (4.3GPa), respectively, compared to pure PET fibers with a modulus of 2.8GPa. Similarly, the nanocomposite fibers of 30 μm diameter have an improved tensile strength of 203 MPa for 0.1wt% CNT fibers which is about 47% greater than the pure PET fibers. In addition, the strain at break and toughness of PET/CNT nanocomposite fibers of 30 μm diameter increased only for the 0.1 wt% CNT addition to PET. The low content of 0.1 wt% CNT in PET matrix enhanced the strain at break and toughness by 33 and 67%, respectively. Strain at break and toughness for pure PET spun fiber was observed to be 3 mm/mm and 266MPa, respectively. The improvement in the modulus of 30 μm diameter fiber is due to the same reason as that of 20 μm diameter fiber but in this case the CNT are partially

aligned. The modulus value obtained here is very far from the expected theoretical value 9GPa. Therefore, CNT are partially aligned in the PET/CNT nanocomposite. During the tensile testing of these fibers, the initially load is not fully transferred from the PET matrix to the CNT because CNT are partially aligned along the direction of stress. Further elongation of PET/CNT nanocomposite fibers with CNT is aligning in the matrix. As a consequence, the CNT held the PET matrix together for increasing its strain at break and toughness [29].

At higher concentration of 1 wt% CNT the modulus of the PET/CNT nanocomposite fibers decreased to 2.12GPa. The nanocomposite fibers with 30 μm diameter have a decrease in yield strength with respect to CNT concentration. However, adding 0.1 wt% CNT had a marginal improvement of about 4% (57MPa) in the yield strength of PET/CNT nanocomposite fibers, compared to pure PET yield strength of 55 MPa. The additions of 0.5 and 1 wt% CNT in PET matrix decrease the yield strength of nanocomposite fibers to 24 and 31 MPa, respectively. Addition of 0.5 and 1wt% CNT in PET/CNT nano composite fibers of 30 μm has decreased the tensile strength to 57 and 61 MPa, respectively. The concentration of 0.5 wt% CNT in PET decreased both strain at break and toughness to 2.0mm/mm and 86MPa, respectively. However, addition of 1wt% CNT has no impact on strain at break of spun PET fibers but decreased the toughness to 128MPa. The adverse impact of high CNT contents is due to agglomeration and formation of voids.

The mechanical properties of nanocomposite fibers with 40μm diameter were observed to decrease with the increase in CNT concentration. The yield strength decreases with increasing CNT. A minimal decrement was observed in the yield strength for addition of 0.1 wt% CNT of 47 MPa, compared to pure PET of 54 MPa. However, drastic decrement was observed in the yield strength of nanocomposite fibers for the addition of 0.5 and 1wt% CNT. It was observed for 0.5 wt% CNT fiber the yield strength decreased to 26MPa and for 1wt% CNT fiber decreased to 29MPa. Likewise, the tensile strength decreases with increasing CNT. A marginal decrement due to addition of 0.1 wt% CNT of 151 MPa, compared to pure PET of 159MPa and, drastic decrement due to addition of 0.5 and 1wt% CNT. It was observed for 0.5 wt% CNT fiber tensile strength decreased to 55MPa and for 1wt% CNT fiber decreased to 50MPa. The nanocomposite-spun fibers of 40 μm diameters had a decreased strain at break with an increase in CNT concentration except for 0.1 wt% CNT concentration. The addition of 0.1 wt% CNT in the PET/CNT nanocomposite spun fiber resulted in no change in strain at break of 7 mm/mm of pure PET nanocomposite-spun fiber. The toughness for nanocomposite-spun fibers with 40 μm diameter decreased with increase in CNT concentration. Addition of 0.1, 0.5 and 1wt% CNT decreased the toughness to 626, 143 and 105MPa, respectively. The decrease in the properties is due to presence of nano flaws agglomeration inside the PET/CNT nanocomposite matrix. In addition, the decrement is also due to random orientation of CNT in the matrix.

In case of nanocomposite fibers with 50 µm diameter, the increase in CNT concentration up to 1wt% had negligible impact on the modulus of PET/CNT nanocomposite fibers. However, significant improvement was observed in modulus of PET/CNT nanocomposite fibers containing 2.7 wt% CNT in PET matrix. An increase of four times the modulus of Pure PET fibers (1.8GPa) was observed. Furthermore, PET/CNT nanocomposite fibers 50µm diameters have similar effect of CNT on yield strength. It is noticed that yield strength of nanocomposite fibers containing very low percentage 0.1 wt% CNT into PET matrix enhanced by about 17% (49MPa), compared to pure PET fibers 42MPa. However, adding above 0.1wt% CNT concentration decreases the yield strength of these fibers. A low concentration of 0.1 wt% CNT enhanced the tensile strength of pure PET fibers (107MPa) by 12% (120MPa) whereas other concentration such as 0.5, 1.0 and 2.7 wt% CNT deteriorate the tensile strength. The nanocomposite fibers with 50 µm diameters have an increment in strain at break and toughness of 0.1wt% CNT, and a decrement in both the properties for higher concentrations of CNT. An increase of about 11% (10.0) in strain at break and an improvement of 26% (689MPa) in toughness is achieved with 0.1wt% CNT. At higher concentrations of CNT, the strain at break and toughness decreased due to the increase in stiffness of the PET/CNT nanocomposite spun fibers.

Low CNT concentration of 0.1 and 0.5 wt% CNT in PET/CNT nanocomposite spun fibers have shown good spinnability, reaching a minimum diameter of about 20µm. The alignment and good distribution of CNT was achieved for low concentration of 0.1 and

0.5wt% CNT. Recent studies [10, 23, 29, 35] emphasised the importance of good alignment of CNT and its positive effect on the mechanical properties of PET/CNT nanocomposite fibers. In addition, the increment in the tensile strengths is due to good bonding between the CNT and PET matrix. The increase in CNT concentration resulted in agglomeration of CNT in the PET matrix. The void formation around the agglomerated CNT decreased the mechanical properties of the spun fibers.

Table 4.1 summarizes the influence of parameters on mechanical properties of PET/CNT nanocomposite fibers.

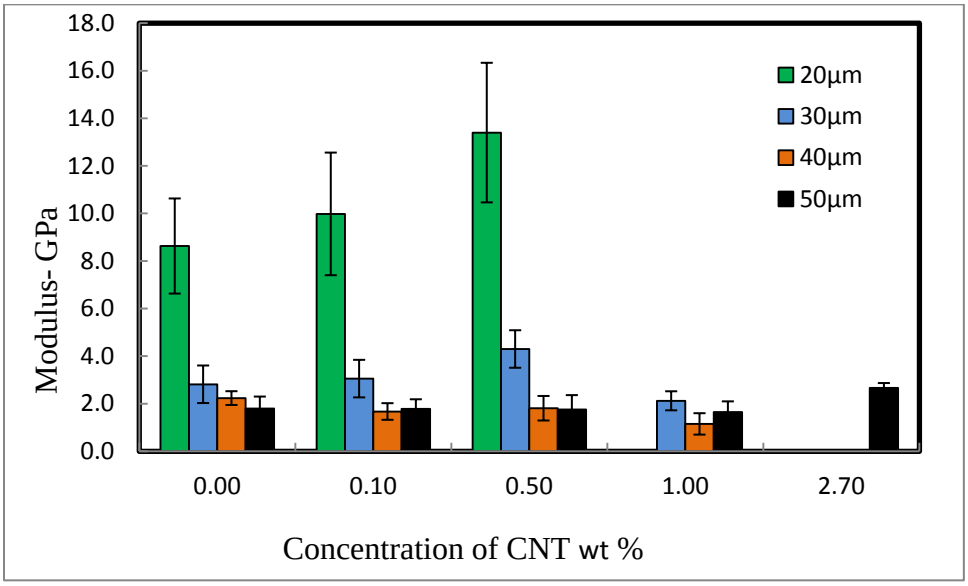

Figure 4.31 Influence of CNT concentration on the modulus of spun PET/CNT nanocomposite fibers.

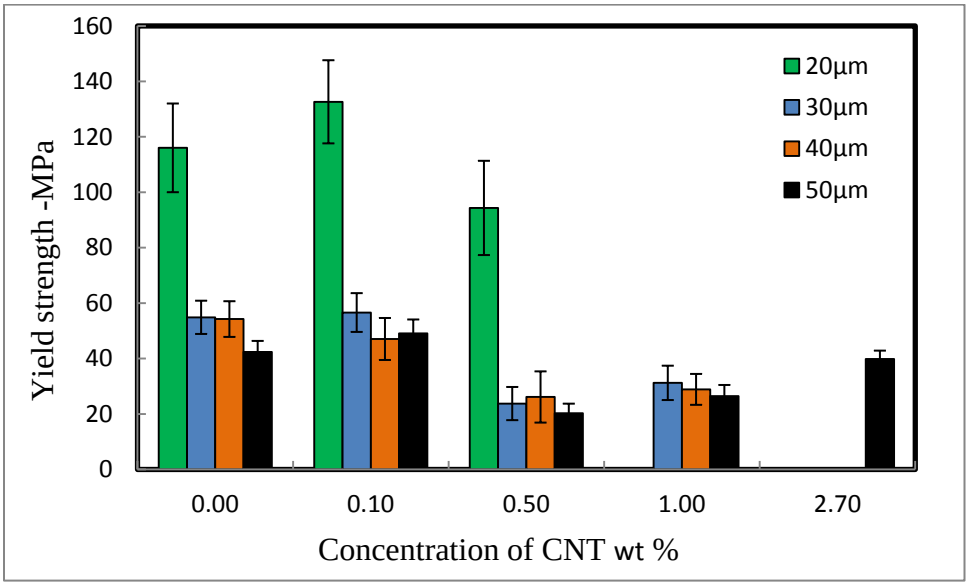

Figure 4.32 Influence of CNT concentration on the yield strength of spun PET/CNT nanocomposite fibers.

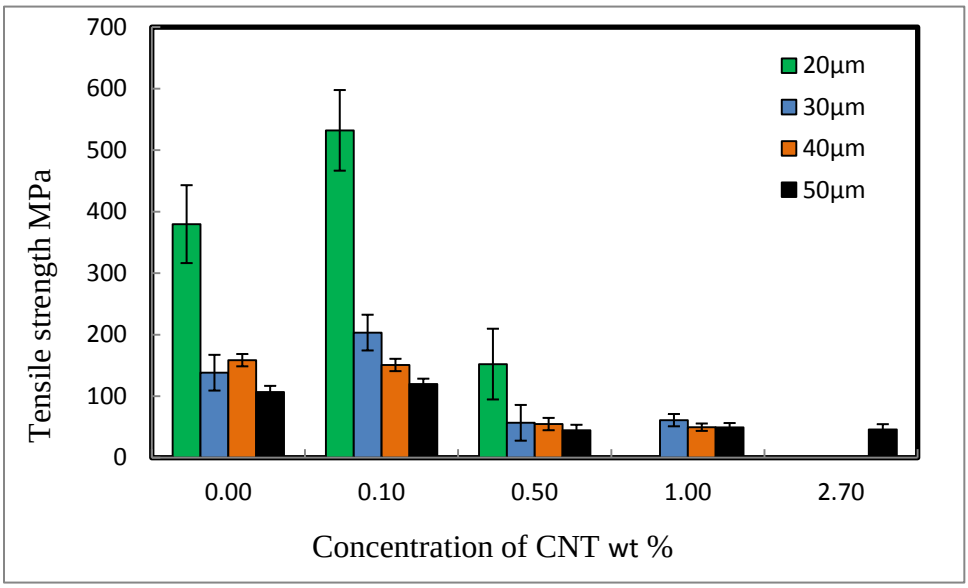

Figure 4.33 Influence of CNT concentration on the tensile strength of spun PET/CNT nanocomposite fibers.

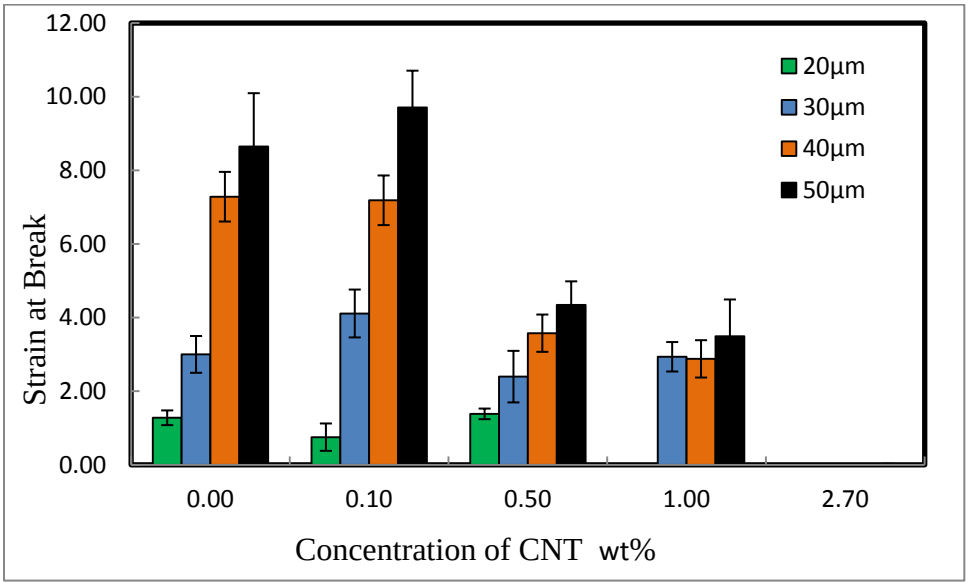

Figure 4.34 Influence of CNT concentration on the strain at break of spun PET/CNT nanocomposite fibers.

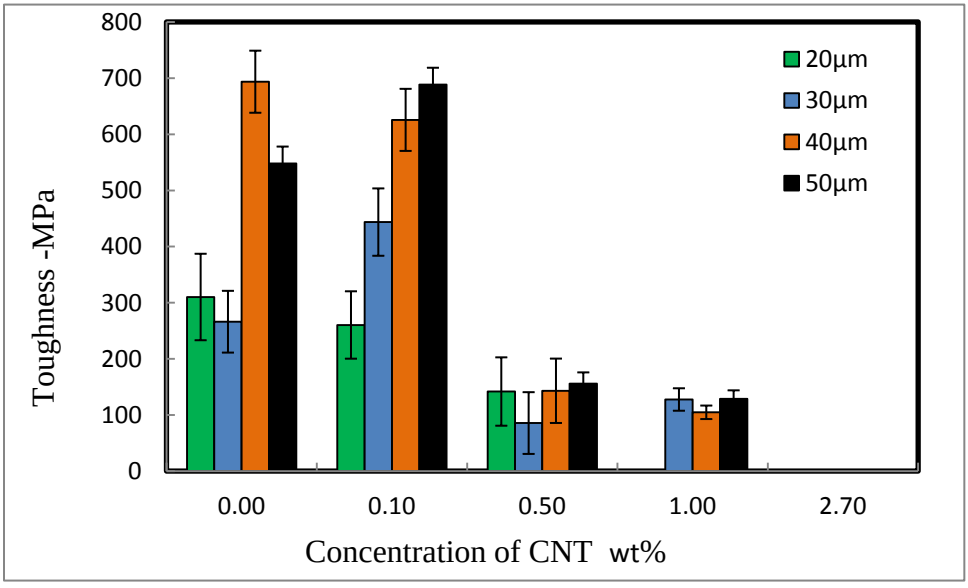

Figure 4.35 Influence of CNT concentration on the toughness of spun PET/CNT nanocomposite fibers.

Table 4.1 Averaged Mechanical Properties of PET/CNT nanocomposite fibers

Parameters		Young's Modulus (GPa)	Yield strength (MPa)	Tensile Strength (MPa)	Strain at break	Toughness (MPa)
Die Temperatures(˚C)	265	1.65	33	81	9.55	445
	280	1.75	30	78	9.21	414
	295	2.10	31	70	8	352
Spinning Speed(m/min)	500	2.1	31	61	3	128
	409	1.5	29	54	3	114
	323	1.1	29	50	3	105
	243	1.6	26	49	3	129
	190	1.4	25	47	4	132
CNT Concentration (wt%) on Extruded PET/CNT nanocomposite Fibers	0	1.62	35	51	3.97	157
	0.1	1.66	30	97	10.85	604
	0.5	1.66	34	78	10.92	556
	1	1.75	30	78	9.21	414
	2.7	1.94	45	65	6.86	314
	3	1.88	46	59	5.97	261
	7.5	4.40	54	67	0.04	1.48
CNT Concentration (wt%) on Spun PET/CNT nanocomposite Fibers- 20µm	0	8.6	116	380	1.28	310
	0.1	10.0	133	532	0.75	260
	0.5	13.4	94	152	1.38	142
CNT Concentration (wt%) on Spun PET/CNT nanocomposite Fibers- 30µm	0.0	2.82	55	138	3	266
	0.1	3.05	57	203	4	444
	0.5	4.30	24	57	2	86
	1.0	2.12	31	61	3	128
CNT concentration (wt%) on spun PET/CNT nanocomposite Fibers- 40µm	0.0	2.23	54	159	7	694
	0.1	1.67	47	151	7	626
	0.5	1.81	26	55	4	143
	1.0	1.15	29	50	3	105
CNT concentration (wt%) on spun PET/CNT nanocomposite Fibers- 50µm	0.0	1.8	42.4	106.7	8.6	548.1
	0.1	1.8	49.1	119.8	9.7	688.6
	0.5	1.8	20.3	44.5	4.3	155.9
	1.0	1.6	26.5	49.3	3.5	128.9
	2.7	2.7	39.9	45.9	0.0	0.6

CHAPTER 5

CONCLUSIONS

This chapter of the thesis is divided into five sections. In the first four sections, the conclusions corresponding to the results in the previous sections are presented.

5.1 Die Temperature Effect

The processiblity of PET/CNT nanocomposite fibers containing 1 wt% CNT with respect to die temperature was studied. The present study investigated the influence of different die temperatures on the processiblity, mechanical properties and the distribution and alignment of CNT in PET/CNT nanocomposite fibers. The PET/CNT nanocomposite fibers were melt extruded through a die at different temperatures of 265, 280 and 290˚C, using melt extrusion technique. The mechanical properties of the PET/CNT nanocomposite fibers were evaluated using tensile tests. Tensile result showed that the die temperature has little effect on the mechanical properties except the modulus of the extruded PET/CNT (1wt %) nanocomposite fibers. The little effect on the mechanical properties was expected as the die temperatures would not affect the distribution of CNT in the fiber as the CNT has already been mixed in the PET matrix before reaching the

extrusion die. However, the fibers obtained at die temperature 290˚C showed high modulus of 2.1 GPa i.e. 27% and 20% higher than the values obtained for die temperatures 265 and 280˚C, respectively. At 290˚C, the increment in the modulus compared other temperatures is attributed to good alignment of CNT in PET matrix. Fibers extruded at different die temperatures were melt spun using a winder to evaluate the effect of die temperature on spinnability. The spinnability of the fibers was correlated to the diameter of the spun fibers. Smallest diameter fibers with the average diameter of 30 µm were produced at die temperature of 280 °C.

5.2 Melt Spinning Effect

Melt spinning of PET/CNT nanocomposite at different spinning speeds in the range of 190m/min to 500 m/min at die temperature 280˚C was studied. Nanocomposite fibers with average diameter in the range of 32 µm to 51µm were obtained. It was observed that the fibers spun at highest speed of 500m/min showed better modulus compared to fibers spun at lower speeds. Fibers at this speed have the average modulus value of 2.12 GPa showing 50% enhancement in modulus value compared to the PET/CNT nanocomposite fibers obtained at the lowest spinning speed 190 m/min. Average yield strength of 31MPa was obtained at spinning speed of 500 m/min. This value is 24% better than the yield strength of fibers obtained at 190m/min. An improvement of 30% in tensile strength of nanocomposite fibers was observed at highest speed of 500m/min compared to lowest speed of 190m/min. The distribution and alignment of CNT in the PET matrix was observed using SEM.

5.3 CNT Concentration Effect

The influence of carbon nanotube (CNT) concentration on the mechanical properties of extruded and spun PET/CNT nanocomposite fibers was studied. Different CNT contents in the range of 0.1 to 7.5wt% were added to PET using a twin screw extruder and were in accordance with the TG DSC results. Aligned CNT found to have improved the mechanical properties by mechanical drawing through melt spinning of these fibers. The extruded and spun nanocomposite fibers were tested for tensile properties. A very low content of 0.1wt% CNT has enhanced the tensile strength of extruded fibers by 90%, compared to extruded pure PET fibers (51MPa) (Figure 4.28). Furthermore, significant enhancements in strain-at-break and toughness by about 170% (Figure 4.29) and 280% (Figure 4.30), respectively, was achieved. The spun fibers of 20 μm diameter with low CNT content of 0.1wt% CNT have shown remarkable increment of about 16% in the modulus, compared to pure PET spun fibers with a modulus of 8.6 GPa. An improvement of 40% (532MPa) in tensile strength of PET/CNT nanocomposite spun fibers was achieved, compared to pure PET fibers of 380MPa. The PET/CNT nanocomposite fibers of 50 μm diameter had good toughness of about 26% (689MPa) improvement. The improvements in the mechanical properties were based on the good mixing, distribution and alignment of CNT in PET/CNT nanocomposite fibers was represented in the SEM micrographs.

CHAPTER 6

FUTURE WORK

Include the followings:

1. Based on the conclusions of the present study it was observed that the alignment of CNT in fine PET/CNT nanocomposite fibers has enhanced the mechanical properties, compared to extruded fibers. The improvement in the mechanical properties of extruded fibers can be further improved by drawing these fibers. Therefore, the study of drawing effect on the mechanical properties of extruded PET/CNT nanocomposite fibers can considered for future work.
2. The better and detail analysis on molecular orientation and CNT alignment in extruded and fine PET/CNT nanocomposite fibers can be studied using Raman spectroscopy and TEM.
3. The interfacial bonding can be improved using modified CNT in PET/CNT nanocomposite fibers. CNT can be modified with acid or functional or both groups.
4. Though twin screw extruder succeeded in obtaining good distribution of CNT in PET/CNT nanocomposite fibers still many voids were observed on the fracture surface of PET/CNT nanocomposite fibers due to limitation of the twin screw

extruder. Twin screw extruder cannot develop high pressure inside the extruder which required for avoiding voids in the PET/CNT nanocomposite fibers. Thus, in order to produce good quality of PET/CNT nanocomposite fibers two step extrusion process can be done. First using twin screw extruder the PET/CNT nanocomposite pellets of required compositions can be produced. Other using single screw extruder the PET/CNT nanocomposite fibers can be produced from these pellets.

NOMENCLATURE

DR	Draw Ratio
DSC	Diferential Scanning Calorimetry
FTIR	Fourier Transformn Infrared Spectroscopy
SEM	Scanning Electron Microscope
TEM	Tranmission Electron Microscope
TG-DSC	Thermogravimetry- Differential Scanning Calorimetry

Polymer Matrix

LLDPE	Linear Low density Polyethylene
PA 12	Polyamide(PA) 12
PAN	Polyacrylonitrile
PBT	Polybutylene
PE	Polyethylene
PEN	Poly (ethylene 2,6 naphthalate)
PET	Poly(ethylene) Teraphthalate
PP	Polypropylene
PVA	Poly Vinyl Alcohol

Nanomaterial

CNF	Carbin nanofibers
CNT	Carbon nanotubes
f-CNT	Functionalised CNT with Functioinal groups
MWCNT	Multi wall CNT
P-CNT	Pristine (pure)-CNT
SWCNT	Single Wall CNT

REFERENCES

[1] T. A. Osswald, Polymer processing fundamentals: Hanser Gardner Pubns, 1998.

[2] J. MclNTYRE, "The Historical Development of Polyesters," Modern polyesters: chemistry and technology of polyesters and copolyesters, p. 1, 2003.

[3] F. Fourné, Synthetic fibers: machines and equipment, manufacture, properties: handbook for plant engineering, machine design, and operation: Hanser Gardner Publications, 1999.

[4] P. Pattabiraman, et al., "Thermal and Mechanical properties of recycled PET and its blends," vol. 8, p. 301, 2005.

[5] H. Ma, et al., "Processing, structure, and properties of fibers from polyester/carbon nanofiber composites," Composites Science and Technology, vol. 63, pp. 1617-1628, 2003.

[6] P. Davies, et al., "Deepwater Mooring With High Stiffness Polyester and PEN Fiber Ropes," 2008.

[7] C. Lechat, et al., "Mechanical behaviour of polyethylene terephthalate & polyethylene naphthalate fibres under cyclic loading," Journal of Materials Science, vol. 41, pp. 1745-1756, 2006.

[8] T. Ochi, et al., "Development of recycled PET fiber and its application as concrete-reinforcing fiber," Cement and Concrete Composites, vol. 29, pp. 448-455, 2007.

[9] S. Iijima, "Helical microtubules of graphitic carbon," Nature, vol. 354, pp. 56-58, 1991.

[10] M. Saeedeh, et al., "Structure and properties of melt-spun PET/MWCNT nanocomposite fibers," Polymer Engineering & Science, vol. 50, pp. 1956-1968, 2010.

[11] O. Breuer and S. Uttandaraman, "Big returns from small fibers: A review of polymer/carbon nanotube composites," Polymer Composites, vol. 25, pp. 630-645, 2004.

[12] A. Krishnan, et al., "Young's modulus of single-walled nanotubes," Physical Review B, vol. 58, pp. 14013-14019, 1998.

[13] J. N. Coleman, et al., "Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites," Carbon, vol. 44, pp. 1624-1652, 2006/8// 2006.

[14] J. E. Mark, Physical properties of polymers handbook: Springer Verlag, 2007.

[15] J. Y. Kim, et al., "Influence of modified carbon nanotube on physical properties and crystallization behavior of poly(ethylene terephthalate) nanocomposite," Polymer Composites, vol. 31, pp. 858-869, 2010.

[16] Z. Li, et al., "Microstructure of carbon nanotubes/PET conductive composites fibers and their properties," Composites Science and Technology, vol. 66, pp. 1022-1029, 2006/6// 2006.

[17] K. Anoop Anand, et al., "Carbon nanotubes induced crystallization of poly(ethylene terephthalate)," Polymer, Special issue in honour of James McGrath, vol. 47, pp. 3976-3980, 2006/5/17/ 2006.

[18] S. Mun, et al., "Poly (ethylene terephthalate) nanocomposite fibers with functionalized multiwalled carbon nanotubes via in situ polymerization," Journal of Applied Polymer Science, vol. 109, pp. 638-646, 2008.

[19] T. Gomez-del Rio, et al., "Influence of single-walled carbon nanotubes on the effective elastic constants of poly(ethylene terephthalate)," Composites Science and Technology, vol. 70, pp. 284-290, 2010/2// 2010.

[20] Y. Wang, et al., "Morphology, crystallization, and mechanical properties of poly(ethylene terephthalate)/multiwall carbon nanotube nanocomposites via <I>in situ</I> polymerization with very low content of multiwall carbon nanotubes," Journal of Applied Polymer Science, vol. 104, pp. 3695-3701, 2007.

[21] Y. Gao, et al., "Functionalized multi-walled carbon nanotubes improve nonisothermal crystallization of poly(ethylene terephthalate)," Polymer Testing, vol. 27, pp. 179-188, 2008/4// 2008.

[22] P. Carine, et al., "Influence of the spinning conditions on the structure and properties of polyamide 12/carbon nanotube composite fibers," Journal of Applied Polymer Science, vol. 114, pp. 3515-3523, 2009.

[23] K. Jun Young, et al., "Crystallization behaviors and mechanical properties of poly(ethylene 2,6-naphthalate)/multiwall carbon nanotube nanocomposites," Polymer Engineering & Science, vol. 47, pp. 1715-1723, 2007.

[24] T. W. Ebbesen, Carbon nanotubes: preparation and properties: CRC, 1997.

[25] Kwiatkowska M, et al., "The in-situ sysnthesis of polybutylene terephthalate/carbon nanotube composites," Rev. Adv. Mat.Sci, vol. 12, pp. 154-159, 2005.

[26] E. Muñoz, et al., "Multifunctional Carbon Nanotube Composite Fibers," Advanced Engineering Materials, vol. 6, pp. 801-804, 2004.

[27] T. Mikolajczyk, et al., "Effect of spinning conditions on the mechanical properties of polyacrylonitrile fibers modified with carbon nanotubes," Journal of Applied Polymer Science, vol. 115, pp. 3628-3635, 2010.

[28] S. Kumar, et al., "Fibers from polypropylene/nano carbon fiber composites," Polymer, vol. 43, pp. 1701-1703, 2002.

[29] K. Mezghani, et al., "Influence of carbon nanotube (CNT) on the mechanical properties of LLDPE/CNT nanocomposite fibers," Materials Letters, vol. 65, pp. 3633-3635, 2011.

[30] C. Perrot, et al., "Influence of the spinning conditions on the structure and properties of polyamide 12/carbon nanotube composite fibers," Journal of Applied Polymer Science, vol. 114, pp. 3515-3523, 2009.

[31] T. D. Fornes, et al., "Morphology and properties of melt-spun polycarbonate fibers containing single- and multi-wall carbon nanotubes," Polymer, vol. 47, pp. 1704-1714, 2006/2/22/ 2006.

[32] A. B. Sulong, et al., "Process optimization of melt spinning and mechanical strength enhancement of functionalized multi-walled carbon nanotubes reinforcing polyethylene fibers," Composites Part B: Engineering, vol. 42, pp. 11-17, 2011.

[33] K. Jun Young, et al., "Influence of modified carbon nanotube on physical properties and crystallization behavior of poly(ethylene terephthalate) nanocomposite," Polymer Composites, vol. 31, pp. 858-869, 2010.

[34] J. Y. Kim, et al., "Mechanical reinforcement and crystallization behavior of poly(ethylene 2,6-naphthalate) nanocomposites induced by modified carbon nanotube," Composites Part A: Applied Science and Manufacturing, vol. 40, pp. 45-53, 2009/1// 2009.

[35] V. K. Rangari, et al., "Fabrication and characterization of high strength Nylon-6/Si3N4 polymer nanocomposite fibers," Materials Science and Engineering: A, vol. 500, pp. 92-97, 2009/1/25/ 2009.

VITAE

Name	:	Mohammed Riyazuddin Farooqui
Address	:	H.No. 19-4-279/S/9, Salehein Colony, Bahadurpura, Near Zoo park, Hyderbad, A.P., India
Telephone	:	+966-535915404
Date of Birth	:	21-08-1986
Nationality	:	Indian
Languages	:	English, Urdu, Hindi, Telugu and Arabic (Basic)
Contact Address	:	King Fahd University of Petroleum and Minerals P.O.BOX-8650, Dhahran-31261, Kingdom of Saudi Arabia
Email	:	mdriyazfarooqui@gmail.com, riyazm@kfupm.edu.sa
Education	:	Master of Science (M.S.) April 2012 Mechanical Engineering Department King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia Bachelor of Engineering (B.E.) May 2008 Mechanical Engineering Department Osmania University, Hyderabd, India in 2008.